

THE DIELECTRIC CONSTANT OF A LIQUID

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Summary

Some earlier theories in which attempts have been made to allow for the influence of molecular shape on the static dielectric constant of a liquid are shown to be inaccurate. A general equation is derived for the dielectric constant of a liquid, and this is then applied to a molecular model consisting, in the first instance, of an ellipsoid uniformly polarized in a principal direction, and secondly, to an optically anisotropic ellipsoid; in both cases the surroundings are assumed to form a continuum. The results of this more general approach applied to several substances are more satisfactory than those obtained by the original Onsager theory. The theory is also applied to mixtures, and in the special case of a dilute solution in a non-polar solvent, the equation of Ross and Sack is obtained when the ellipsoid is isotropic. A correlation has been noted in the discrepancies found when the dipole moment of a substance is calculated by means of observations on the pure liquid and on dilute solutions in a non-polar solvent, using the equations derived in the present paper.

I. INTRODUCTION AND DERIVATION OF EQUATION

Several papers have recently been published in which attempts have been made to determine the effects of molecular shape on the dielectric constant of a pure liquid or of a solution. The theory of Raman and Krishnan (1928) falls into this category. Scholte (1949a, 1949b) has suggested extensions to Onsager's (1936) theory of the dielectric constant of a pure liquid to include the case of ellipsoidal molecules. Abbott and Bolton (1952) have considered a liquid consisting of spheroidal molecules, and derived an expression for the static dielectric constant. The case of a dilute solution of a solute consisting of ellipsoidal molecules in non-polar media has been treated by Scholte (1951).

All these authors assume that the electric moment per unit volume, that is, the polarization \mathbf{P} , of a pure liquid, is given by

$$\mathbf{P} = \frac{\epsilon - 1}{4\pi} \mathbf{E} = N \overline{\mathbf{m}_E}, \quad \dots \dots \dots (1)$$

where ϵ is the static dielectric constant of the liquid, \mathbf{E} is the strength of the applied field in the liquid, $\overline{\mathbf{m}_E}$ is the mean value of the component of the total moment of a single molecule in the direction of \mathbf{E} , and N is the number of molecules per unit volume.

However, the static dielectric constant is a macroscopic property of a liquid and we are thus concerned with a specimen whose dimensions are large compared to those of a single molecule. We must therefore consider the polarization of a spherical specimen, sufficiently large to exhibit the macroscopic

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properties of the liquid. Then, if \mathbf{M} is the moment of this sphere in the direction of \mathbf{E} , equation (1) becomes

$$\mathbf{P} = \frac{\epsilon - 1}{4\pi} \mathbf{E} = \frac{\mathbf{M}}{v}, \quad \dots \dots \dots (2)$$

where v is the volume of the sphere.

Now \mathbf{M} is not equal to $Nv\overline{\mathbf{m}_e}$, except for the particular case of spherical molecules. This is clearly seen when the components of \mathbf{M} are analysed. Consider the moment of a spherical specimen due to a single solute molecule in a non-polar solvent of dielectric constant ϵ . Then if we suppose the molecule is at the centre of our spherical specimen, the moment will consist of: (i) the actual moment of the molecule in the medium, that is, μ , where μ itself consists of the permanent "gas" moment together with the moment induced in the solute molecule by its reaction field; and (ii) the moment induced in the surrounding medium by the solute molecule, that is,

$$-\frac{\epsilon - 1}{4\pi} \int \text{grad } \varphi \, dv,$$

where φ is the potential, and the integration extends over the volume bounded by the solute molecule itself and the outer boundary of the large sphere. Now effect (ii) will contribute to \mathbf{M} if the shape of the solute molecule is non-spherical.

If μ^* is the total moment of the sphere due to the permanent polarization of a single solute molecule at its centre, then the Appendix to Kirkwood's (1939) paper shows that the moment will still be μ^* when the molecule is not centrally placed, provided it is not close to the outer boundary. Now the proportion of those molecules present which are close to the boundary can be made as small as we please by increasing the radius of the sphere. Thus we can say that

$$\mathbf{M} = Nv\mu^* \overline{\mathbf{u} \cos \theta} + \frac{3\epsilon(n^2 - 1)v}{(2\epsilon + n^2)4\pi} \mathbf{E}, \quad \dots \dots \dots (3)$$

where the bar signifies a mean value, and where \mathbf{u} is the unit vector in the direction of the permanent moment of the molecule, and θ is the angle between \mathbf{u} and \mathbf{E} . The second term of \mathbf{M} in (3) is the moment induced in the specimen; that is, n^2 is the dielectric constant at frequencies so high that the dipoles cannot reach equilibrium and hence n^2 is the square of the "effective" refractive index of the substance, defined by

$${}_nP = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d}, \quad \dots \dots \dots (4)$$

where ${}_nP$ is the distortion polarization of the substance.

Thus, from (2) and (3),

$$\frac{(2\epsilon + 1)(\epsilon - n^2)}{(2\epsilon + n^2)} \mathbf{E} = 4\pi N\mu^* \overline{\mathbf{u} \cos \theta}. \quad \dots \dots \dots (5)$$

Now μ^* will depend on the actual moment of the molecule, which in turn is a function of μ_0 , the "gas" value of the moment (that is, μ when there is no reaction field), so that we may write

$$\mu^* = f\mu_0, \quad \dots \dots \dots (6)$$

where f is a constant depending on the shape and other properties of the molecule.

The mean value of $\cos \theta$, that is, $\overline{\cos \theta}$, is given by $L[-W/kT \cos \theta]$, where $L[x]$ is the Langevin function of x , k is Boltzmann's constant, T the absolute temperature, and W the "orientational" energy of the molecule in the field E .

Now we shall suppose

$$W = -g\mu_0 E \cos \theta, \quad \dots\dots\dots (7)$$

so that, for small applied fields,

$$\overline{\cos \theta} = \frac{g\mu_0}{3kT} E, \quad \dots\dots\dots (8)$$

where g is a constant, and like f , depends on molecular properties.

Hence, from (5), (6), and (8), we have

$$\frac{4\pi N\mu_0^2}{9kT} = \frac{(\epsilon - n^2)(2\epsilon + 1)}{3(2\epsilon + n^2)fg}. \quad \dots\dots\dots (9)$$

II. AN ELLIPSOID AS A MOLECULAR MODEL

For the purpose of evaluating f and g , we shall suppose that the liquid consists of uniformly polarized ellipsoids each of which is surrounded by a continuum, that is, we shall employ the same model as that used by Scholte (1949b, 1951).

Consider a single ellipsoid of semi-axes a , b , and c at the centre of a large spherical specimen. We assume that the material of the ellipsoid possesses a dielectric constant n^2 . Suppose the surroundings of the ellipsoid, which is polarized uniformly in the direction of the a -axis, are continuous and have dielectric constant ϵ . Now

$$\mu^* = \mu + \mu_{\text{induced}}, \quad \dots\dots\dots (10)$$

where μ is comprised of the "gas" moment μ_0 together with a component due to the reaction field R . μ_{induced} is the moment induced in the solvent within the specimen by the polarization of the solute molecule.

The reaction field R is given by (see Scholte 1949a; Abbott and Bolton 1952)

$$R = \frac{3A(1-A)(\epsilon-1)}{[\epsilon-(\epsilon-1)A]abc} \mu u, \quad \dots\dots\dots (11)$$

where A is an "internal field function", defined by (see Ross and Sack 1950)

$$A = \frac{abc}{2} \int_0^\infty \frac{ds}{\sqrt{(s+a^2)^3(s+b^2)(s+c^2)}}, \quad \dots\dots\dots (12)$$

s being a parameter, and μ satisfies

$$\mu = \mu_0 + \alpha_a R,$$

where α_a is the polarizability of the ellipsoid in a direction parallel to the a -axis.

Thus

$$\mu = \frac{[1+(n^2-1)A][\epsilon-(\epsilon-1)A]}{[\epsilon+(n^2-\epsilon)A]} \mu_0, \quad \dots\dots\dots (13)$$

for

$$\alpha_a = \frac{n^2 - 1}{3[1 + (n^2 - 1)A]} abc, \text{ (see Scholte 1949a). } \dots (14)$$

To calculate the moment induced in the surrounding solvent, the field outside a uniformly polarized ellipsoid is required. Now Stratton (1941) derives an expression for the potential at a point outside a dielectric ellipsoid in a uniform field \mathbf{E}_0 applied parallel to the a -axis. His result for the potential at a point on an ellipsoid whose semi-axis corresponding to a is $\sqrt{a^2 + \beta}$ and which is confocal with the original, is

$$\varphi^+ = -E_0 x - \frac{abc}{\varepsilon + (n^2 - \varepsilon)A} \int_0^\beta \frac{ds}{\sqrt{(s+a^2)^2(s+b^2)(s+c^2)}},$$

x being the distance of the point from the plane of the b - and c -axes.

The disturbing potential due to the polarization of the ellipsoid is $\varphi^+ + E_0 x$, that is,

$$E_0 x \frac{n^2 - \varepsilon}{\varepsilon + (n^2 - \varepsilon)A} \frac{abc}{2} \int_\beta^\infty \frac{ds}{\sqrt{(s+a^2)^2(s+b^2)(s+c^2)}}.$$

If the field \mathbf{E}_0 were now removed, leaving the ellipsoid still polarized, the potential outside would be the above disturbing potential, and the polarization of the ellipsoid would be

$$\frac{(n^2 - 1)\mathbf{E}' - (\varepsilon - 1)\mathbf{E}_0}{4\pi},$$

where \mathbf{E}' is the field originally inside the ellipsoid, that is,

$$\mathbf{E}' = \frac{\varepsilon}{\varepsilon + (n^2 - \varepsilon)A} \mathbf{E}_0.$$

The actual moment of the ellipsoid is thus $\frac{4}{3}\pi abc \times \text{polarization}$, that is,

$$\frac{(n^2 - \varepsilon)[\varepsilon - (\varepsilon - 1)A]abc}{3[\varepsilon + (n^2 - \varepsilon)A]} \mathbf{E}_0.$$

Thus for a moment μ , the potential outside is given by

$$\varphi = \frac{3\mu x}{2[\varepsilon - (\varepsilon - 1)A]} \int_\beta^\infty \frac{ds}{\sqrt{(s+a^2)^2(s+b^2)(s+c^2)}}.$$

The electric field \mathbf{E} is equal to $-\text{grad } \varphi$, so that the total moment induced in the solvent in the spherical specimen will be

$$\begin{aligned} \mu_{\text{induced}} &= \frac{\varepsilon - 1}{4\pi} \int_{\text{vol. of solvent}} \mathbf{E} dv = -\frac{\varepsilon - 1}{4\pi} \int \text{grad } \varphi dv \\ &= \frac{\varepsilon - 1}{4\pi} \left[\int_{S_1} \varphi \mathbf{n} dS - \int_S \varphi \mathbf{n} dS \right], \text{ (by a generalized Green's theorem),} \end{aligned}$$

where S_0 is the surface similar to, and just outside, the ellipsoid, S is the surface of the spherical specimen, and \mathbf{n} is the unit vector in the direction of the outward normal to the element of surface dS .

Now since the radius of the specimen, r , is very much greater than a , b , and c ,

$$\int_{\beta}^{\infty} \frac{ds}{\sqrt{(s+a^2)(s+b^2)(s+c^2)}}$$

can, in the second integral, be replaced by

$$\int_{r^2-a^2}^{\infty} \frac{ds}{\sqrt{(s+a^2)^3}}$$

that is, by $2/3r^3$.

Thus

$$\begin{aligned} \int_S \varphi \mathbf{n} dS &= \frac{\mu}{[\epsilon - (\epsilon - 1)A]r^3} \int x \mathbf{n} dS \\ &= \frac{\mu \mathbf{u}}{[\epsilon - (\epsilon - 1)A]r^3} \int_{\text{vol.}} dv = \frac{4\pi\mu \mathbf{u}}{3[\epsilon - (\epsilon - 1)A]}, \end{aligned}$$

since \mathbf{u} (that is, $\text{grad } x$) is the unit vector in the direction of the a -axis.

Again,

$$\int_{S_0} \varphi \mathbf{n} dS = \frac{3A\mu}{[\epsilon - (\epsilon - 1)A]abc} \int_{S_0} x \mathbf{n} dS,$$

since $\beta=0$ on the surface of the ellipsoid.

Hence

$$\begin{aligned} \int_{S_0} \varphi \mathbf{n} dS &= \frac{3A\mu \mathbf{u}}{[\epsilon - (\epsilon - 1)A]abc} \int_{\text{vol.}} dv \\ &= \frac{4\pi A}{[\epsilon - (\epsilon - 1)A]} \mu \mathbf{u}. \end{aligned}$$

Thus

$$\mu_{\text{induced}} = \frac{(\epsilon - 1)(A - \frac{1}{3})}{[\epsilon - (\epsilon - 1)A]} \mu, \quad \dots \quad (15)$$

and therefore, by (10) and (13),

$$\mu^* = \frac{(2\epsilon + 1)[1 + (n^2 - 1)A]}{3[\epsilon + (n^2 - \epsilon)A]} \mu_0. \quad \dots \quad (16)$$

Thus, in (6),

$$f = \frac{(2\epsilon + 1)[1 + (n^2 - 1)A]}{3[\epsilon + (n^2 - \epsilon)A]}. \quad \dots \quad (17)$$

Now W is equal to $-\mu \mathbf{u} \cdot \mathbf{G}$, where \mathbf{G} is the cavity field. For our model

$$\mathbf{G} = \frac{\epsilon}{\epsilon - (\epsilon - 1)A} \mathbf{E}$$

(see Stratton 1941), so that, by (7) and (13),

$$g = \frac{\epsilon[1+(n^2-1)A]}{[\epsilon+(n^2-\epsilon)A]} \dots\dots\dots (18)$$

Thus, on substituting in (9) the above values for f and g , we have, in the case of our particular model,

$$\frac{4\pi N\mu_0^2}{9kT} = \frac{(\epsilon-n^2)[\epsilon+(n^2-\epsilon)A]^2}{\epsilon(2\epsilon+n^2)[1+(n^2-1)A]^2} \dots\dots\dots (19)$$

or, since

$$N = \frac{N_d}{M},$$

where N is Avogadro's number, the "true" orientation polarization of the substance is found to be

$${}_oP = \frac{4\pi N\mu_0^2}{9kT} = \frac{(\epsilon-n^2)[\epsilon+(n^2-\epsilon)A]^2 M}{\epsilon(2\epsilon+n^2)[1+(n^2-1)A]^2 d} \dots\dots\dots (20)$$

III. APPLICATION TO EXPERIMENTAL DATA

Equation (20) may be applied to pure liquid data for the purpose of determining μ_0 . This has been done for nine different liquids at 25 °C., and the data and results are summarized in Table 1. The A 's were determined from the

TABLE 1
DIPOLE MOMENT VALUES CALCULATED FROM PURE LIQUID DATA AT 25 °C.

Substance	A	ϵ	n^2	d	μ_0 by (20)	μ_0 by (21)	μ_{gas} Found
CH ₃ Cl ..	0.25	9.68	1.929	0.8785	2.04	1.76	1.86
CH ₂ Cl ₂ ..	0.36	8.93	2.349	1.3175	1.50	1.58	1.57
CHCl ₃ ..	0.46	4.724	2.368	1.4790	0.91	1.10	1.01
SO ₂ ..	0.36	13.20	1.911	1.369	1.81	1.90	1.62
Paraldehyde	0.59	12.93	2.499	0.9896	1.55	2.72	1.44
N(CH ₃) ₃ ..	0.47	2.44	1.808	0.6267	0.66	0.74	0.64
C ₆ H ₅ Cl ..	0.18	5.612	2.554	1.1011	1.76	1.35	1.73
C ₆ H ₅ NO ₂	0.17	34.89	2.633	1.1986	5.83	3.96	4.24
C ₆ H ₅ CN ..	0.16	25.20	2.329	1.0013	5.23	3.58	4.39

molecular dimensions (that is, the A 's, B 's, and C 's) of Angyal, Barclay, and Le Fèvre (1950), by referring to the graphs of Osborn (1945). The other constants are those used by Buckingham and Le Fèvre (1952). The values of μ_0 calculated by the Onsager (1936) equation, namely,

$${}_oP = \frac{4\pi N\mu_0^2}{9kT} = \frac{(\epsilon-n^2)(2\epsilon+n^2)M}{\epsilon(n^2+2)^2 d} \dots\dots\dots (21)$$

are included for comparative purposes.

Before discussing the above values it may be of interest to evaluate the results for an optically anisotropic molecule.

Suppose the ellipsoid consists of material whose polarizability in the direction of the dipole (that is, along the a -axis) is α_a , where

$$\alpha_a = \frac{n_a^2 - 1}{3[1 + (n_a^2 - 1)A]} abc. \quad (22)$$

Equations (4) and (9) still apply, but (17) and (18) now become

$$f = \frac{(2\varepsilon + 1)[1 + (n_a^2 - 1)A]}{3[\varepsilon + (n_a^2 - \varepsilon)A]}, \quad (23)$$

and

$$g = \frac{\varepsilon(1 + (n_a^2 - 1)A)}{[\varepsilon + (n_a^2 - \varepsilon)A]}. \quad (24)$$

Thus the orientation polarization, on the basis of this more general model, is

$${}_oP = \frac{4\pi N\mu_0^2}{9kT} = \frac{(\varepsilon - n^2)[\varepsilon + (n_a^2 - \varepsilon)A]^2 M}{\varepsilon(2\varepsilon + n^2)[1 + (n_a^2 - 1)A]^2 d}. \quad (25)$$

For the purpose of evaluating n_a^2 , use may be made of the α_a/α values of Stuart and Volkmann (1933). We shall assume that

$${}_dP_a = \frac{\alpha_a}{\alpha} {}_dP = \frac{n_a^2 - 1}{3[1 + (n_a^2 - 1)A]} \frac{M}{d}, \quad (26)$$

so that

$$n_a^2 = 1 + \frac{1}{(M/3{}_dP_a d) - A}. \quad (27)$$

Table 2 shows the required data and the calculated values of μ_0 according to equations (20), (21), and (25) over a considerable temperature range for

TABLE 2
CALCULATED DIPOLE MOMENTS OF CHCl_3 AND $\text{C}_6\text{H}_5\text{NO}_2$ AT SEVERAL TEMPERATURES

Substance	Temp. (°C.)	ε	d	n^2	n_a^2	μ_0 by (20)	μ_0 by (21)	μ_0 by (25)	μ_{gas}
CHCl_3	-20	5.512	1.5635	2.485	2.27 ₉	0.88	1.07	0.91	1.01
	20	4.813	1.4895	2.382	2.18 ₆	0.91	1.10	0.94	
	50	4.310	1.4315	2.305	2.11 ₆	0.92	1.10	0.95	
$\text{C}_6\text{H}_5\text{NO}_2$	10	37.85	1.213	2.663	2.96 ₂	5.88	3.98	5.66	4.24
	80	26.28	1.143	2.519	2.81 ₅	5.66	3.90	5.45	
	130	20.79	1.09	2.41 ₅	2.71	5.52	3.86	5.32	
	200	15.95	1.02	2.29	2.57	5.42	3.86	5.23	

chloroform and nitrobenzene. These two compounds were selected since they are two of the substances examined by Wilson (1939) for which the ratio of μ_0 (calculated by Onsager's equation) to μ_{gas} did not approach unity as T increased. The dielectric constants and densities quoted are those used by Böttcher (1939),

while the n^2 values have been calculated in accordance with (4). The ${}_D P_a$ values employed were: CHCl_3 20.5, and $\text{C}_6\text{H}_5\text{NO}_2$ 49.8 cc.

The first point to be noted is that the macroscopic n^2 has been employed as the dielectric constant of the ellipsoid. The only justification for this usage is that the surroundings of the molecule have been assumed to be continuous and to possess the macroscopic dielectric constant. Probably the chief cause of the discrepancy between the predictions and observations is due to this somewhat arbitrary choice of n^2 values.

The evidence of Table 1 indicates that while the more general theory is to be preferred to Onsager's, a result obtained from observations on a pure liquid at a single temperature cannot be relied upon as an accurate estimate of μ_{gas} . Thus, while for paraldehyde, trimethylamine, and chlorobenzene the predictions are reasonably satisfactory—being considerably superior to those forecast by (21)—nevertheless in other cases, namely, nitrobenzene and benzonitrile, the more general theory is not better in this respect.

Table 2 clearly shows the superiority of the new equations, for both yield μ_0 values which approach μ_{gas} as T increases. Equation (25), with its allowance for anisotropy, seems preferable to (20).

Thus there appears to be evidence to indicate that a theory embodying allowances for molecular shape and for optical anisotropy adds considerably to the accuracy with which the dielectric properties of pure liquids may be described.

IV. APPLICATION OF THE THEORY TO SOLUTIONS

In the case of a solution containing i components, equation (9) becomes

$$\frac{(2\varepsilon+1)(\varepsilon-n^2)}{3(2\varepsilon+n^2)} = \frac{4\pi}{9kT} \sum N_i (\mu_{0i})^2 f_i g_i, \quad \dots \dots \dots (28)$$

where ε and n^2 are the dielectric constant and the square of the "effective" refractive index of the solution, which contains N_i molecules of the i th species in unit volume, and where the summation extends over all species present. Also, in the case of our particular model,

$$f_i = \frac{(2\varepsilon+1)[1+(n_i^2-1)A_i]}{3[\varepsilon+(n_i^2-\varepsilon)A_i]}, \quad \dots \dots \dots (29)$$

and

$$g_i = \frac{\varepsilon[1+(n_i^2-1)A_i]}{[\varepsilon+(n_i^2-\varepsilon)A_i]}, \quad \dots \dots \dots (30)$$

where n_i is the effective refractive index and A_i the internal field function of the i th component of the mixture.

Thus, from (28), (29), and (30), we have

$$\frac{(\varepsilon-n^2)}{\varepsilon(2\varepsilon+n^2)} = \frac{4\pi}{9kT} \sum N_i \left[\frac{1+(n_i^2-1)A_i}{\varepsilon+(n_i^2-\varepsilon)A_i} \right]^2 (\mu_{0i})^2. \quad \dots \dots \dots (31)$$

In the special case of a solution of a single polar substance in a non-polar solvent, (28) yields

$$\frac{(2\epsilon_{\text{soln.}} + 1)(\epsilon_{\text{soln.}} - n_{\text{soln.}}^2)}{(2\epsilon_{\text{soln.}} + n_{\text{soln.}}^2)} = \frac{4\pi N}{3kT} \mu_0^2 fg, \quad \dots \quad (32)$$

while (31) becomes

$$\frac{\epsilon_{\text{soln.}} - n_{\text{soln.}}^2}{\epsilon_{\text{soln.}}(2\epsilon_{\text{soln.}} + n_{\text{soln.}}^2)} = \frac{4\pi N}{9kT} \left[\frac{1 + (n^2 - 1)A}{\epsilon_{\text{soln.}} + (n^2 - \epsilon_{\text{soln.}})A} \right]^2 \mu_0^2, \quad \dots \quad (33)$$

where there are N solute molecules in unit volume, and where n is the effective refractive index and A the internal field function of a solute molecule.

For a dilute solution in a non-polar medium $\epsilon_{\text{soln.}}$ and $n_{\text{soln.}}^2$ are both nearly equal to ϵ , the dielectric constant of the pure solvent, so that, from (32), we have

$$\epsilon_{\text{soln.}} - n_{\text{soln.}}^2 = \frac{4\pi N}{3kT} \frac{3\epsilon}{2\epsilon + 1} \mu_0^2 fg, \quad \dots \quad (34)$$

and from (33)

$$\epsilon_{\text{soln.}} - n_{\text{soln.}}^2 = \frac{4\pi N}{3kT} \left[\frac{\epsilon[1 + (n^2 - 1)A]}{\epsilon + (n^2 - \epsilon)A} \right]^2 \mu_0^2, \quad \dots \quad (35)$$

Now the Debye equation

$$\frac{\epsilon_{\text{soln.}} - 1}{\epsilon_{\text{soln.}} + 2} - \frac{n_{\text{soln.}}^2 - 1}{n_{\text{soln.}}^2 + 2} = \frac{4\pi N}{9kT} (\mu_s)^2,$$

where μ_s is the "solution" moment of the solute, becomes under these conditions

$$\epsilon_{\text{soln.}} - n_{\text{soln.}}^2 = \frac{4\pi N}{3kT} \left(\frac{\epsilon + 2}{3} \right)^2 (\mu_s)^2, \quad \dots \quad (36)$$

Thus, from (34) and (36), we have

$$\frac{\mu_s}{\mu_0} = \frac{3}{\epsilon + 2} \sqrt{\frac{3\epsilon fg}{2\epsilon + 1}}, \quad \dots \quad (37)$$

For the particular model employed,

$$\frac{\mu_s}{\mu_0} = \frac{3\epsilon[1 + (n^2 - 1)A]}{(\epsilon + 2)[\epsilon + (n^2 - \epsilon)A]}, \quad \dots \quad (38)$$

and this is identical to the equation of Ross and Sack (1950), giving the expected ratio of the "solution" and "gas" moments. Now the above theory yields equation (38) on the assumption that the solute ellipsoid is uniformly polarized. However, the Ross-Sack treatment does not embody this restriction. Their derivation, however, is open to the objection that their use of the relationship

$$\epsilon_{\text{soln.}} - n_{\text{soln.}}^2 = \frac{4\pi N}{3kT} (\mu_e)^2, \quad (\text{see Fröhlich 1949}),$$

where μ_e is the "external" moment of the molecule, that is, μ_e is the moment of a point dipole which produces in the surrounding medium the same field as that of the molecule itself, implies that the field of a polarized ellipsoid can be produced by a point dipole. In general this is not so.

In the case of an optically anisotropic solute, (38) becomes

$$\frac{\mu_s}{\mu_0} = \frac{3\varepsilon[1 + (n_a^2 - 1)A]}{(\varepsilon + 2)[\varepsilon + (n_a^2 - \varepsilon)A]} \quad \dots\dots\dots (39)$$

In Table 3, equations (38) and (39) are applied to solutions of the compounds listed in Table 1, in benzene at 25 °C., so that $\varepsilon = 2.2725$. The observed μ_s/μ_{gas} values are those used by Buckingham and Le Fèvre (1952).

TABLE 3
EQUATIONS (38) AND (39) APPLIED TO SOLUTIONS IN BENZENE AT 25 °C.

Substance	D_a^P (cc.)	n_a^2	μ_s by (38) μ_0	μ_s by (39) μ_0	$\frac{\mu_s}{\mu_{\text{gas}}}$ Found
CH ₃ Cl	16.1	2.06 ₄	0.89 ₉	0.91 ₀	0.91
CH ₂ Cl ₂	—	—	1.03 ₁	—	0.99
CHCl ₃	20.5	2.17 ₃	1.12 ₂	1.10 ₃	1.12
SO ₂	9.7	1.80 ₁	0.98 ₉	0.97 ₈	0.99
Paraldehyde	—	—	1.25 ₀	—	1.30
N(CH ₃) ₃	—	—	1.07 ₂	—	1.34
C ₆ H ₅ Cl	45.4	2.75 ₃	0.87 ₉	0.89 ₀	0.92
C ₆ H ₅ NO ₂	49.8	2.93 ₂	0.87 ₄	0.88 ₉	0.93
C ₆ H ₅ CN	—	—	0.84 ₈	—	0.92*

* The μ_s value of Everard, Kumar, and Sutton (1951) has been used for this substance.

If we assume that the observed values of μ_s/μ_{gas} are subject to experimental errors of at least 2 per cent., then it can be seen that those compounds for which (38) yields values outside this margin are more accurately treated by (39), for example, chlorobenzene and nitrobenzene. The sign of the "solvent effect", that is, $\mu_s - \mu_{\text{gas}}$, is correctly forecast for all substances with the exception of methylene chloride. In this case, however, experimental errors provide a possible excuse, for $\mu_{\text{C}_6\text{H}_6}$ is nearly equal to μ_{gas} .

An interesting observation that can be made from Tables 1 and 2 considered jointly is that the sign of the errors in μ_0 values predicted by (20) and by (38) (in which case $\mu_0 = \mu_s \div (\mu_s/\mu_0)$ is the same for every compound examined. Thus in the case of nitrobenzene a μ_{gas} value greater than the observed 4.24 D is predicted by both (20) and by (38)—both require a higher value for the product *fg*.

V. ACKNOWLEDGMENT

The author wishes to thank Professor R. J. W. Le Fèvre for participating in helpful discussions on the foregoing topics.

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THE DIELECTRIC PROPERTIES OF CRYSTALLINE ALCOHOLS CONTAINING STERICALLY HINDERED HYDROXYL GROUPS

By R. J. MEAKINS*

[Manuscript received November 3, 1952]

Summary

It has been previously suggested that the high dielectric absorption of certain crystalline forms of long-chain alcohols is associated with hydrogen-bonding of the hydroxyl groups. This theory is supported by the results given in the present paper, which show that with other alcohols, in which the hydroxyl groups are sterically hindered, the loss is almost completely eliminated.

The smallest losses are obtained with triphenylcarbinol and cholesterol which both possess hydroxyl groups embedded in a bulky molecular structure. For the former compound, infra-red data from the literature indicate the absence of any appreciable amount of hydrogen-bonding and are thus in agreement with the evidence from dielectric measurements.

High frequency absorption observed in these compounds is considered to be associated with dipole orientation resulting from hindered rotation of the free hydroxyl groups.

The effects of steric hindrance of the hydroxyl group are also observed in *tert.*-butanol.

I. INTRODUCTION

In previous publications (Meakins and Sack 1951; Hamon and Meakins 1952) it has been suggested that the abnormally large dielectric absorption of long-chain alcohols crystallized from the melt is due to the presence of hydrogen-bonded chains of hydroxyl groups capable of reversal. It seemed likely that useful evidence regarding this theory might be obtained by making electrical measurements with other alcohols in which hydrogen-bonding would be hindered by the presence of bulky radicals adjacent to the hydroxyl group. For this programme, the compounds triphenylcarbinol, cholesterol, and *tert.*-butanol were chosen as being especially suitable. The structural formulae of these compounds are shown in Figure 1.

In both triphenylcarbinol and cholesterol the hydroxyl groups are attached to large radicals and are mutually inaccessible compared with the hydroxyl groups in long-chain alcohols. A study of molecular models, approximately to scale, suggests that, although it might be possible for hydrogen-bonding to occur between pairs of hydroxyl groups, the formation of longer hydrogen-bond chains would be prevented by the bulky molecular structures of these compounds.

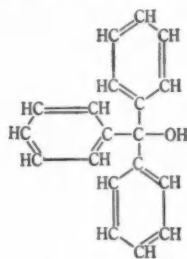
With *tert.*-butanol, reference to molecular models suggests that a crystal structure enabling the formation of hydrogen-bond chains is possible. There

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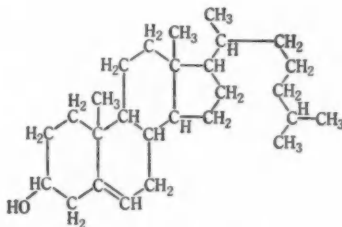
is more hindrance than in normal long-chain alcohols, however, and it might therefore be expected that the extent of hydrogen-bonding, and hence the dielectric loss, would be less.

II. MATERIALS

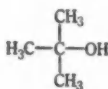
Triphenylcarbinol, m.p. 163 °C., was prepared by the action of methyl benzoate on phenyl magnesium bromide. It was purified by prolonged steam distillation, then by recrystallization from light petroleum (60–80 °C.), and finally from dry benzene.



TRIPHENYLCARBINOL



CHOLESTEROL



tert-BUTANOL

Fig. 1.—Structural formulae of triphenylcarbinol, cholesterol, and *tert*-butanol.

Cholesterol, m.p. 148 °C., was obtained from a commercial product by recrystallization twice from dry benzene.

tert-Butanol, setting pt. 25.4 °C., was prepared from commercial material by drying the latter over calcium oxide and then fractionating through an efficient column. The resulting product was shaken with recently activated alumina and then filtered through sintered glass directly into a dielectric test cell. The latter was sealed by means of a rubber stopper.

III. APPARATUS AND PROCEDURE

Triphenylcarbinol and cholesterol were measured in the form of disks, 5 cm. diameter. These were prepared by melting the crystals under vacuum (1 mm.), allowing to cool, and then grinding the solid to powder. The latter was pressed into disks between steel moulds, as previously described (Meakins and Sack 1951).

For the electrical measurements, the disks were placed between mercury electrodes maintained at 20 °C.

tert.-Butanol is hygroscopic and was therefore measured in a closed dielectric test cell. The measurements were made at -14 and -42°C .

The type of apparatus used for the electrical measurements and the methods of temperature control for the dielectric test cell have been indicated previously (Hamon and Meakins 1952).

IV. RESULTS AND DISCUSSION

(a) Triphenylcarbinol and Cholesterol

The relationship between the dielectric loss factor ϵ'' and the frequency f for triphenylcarbinol and cholesterol is shown in Figure 2, in comparison with

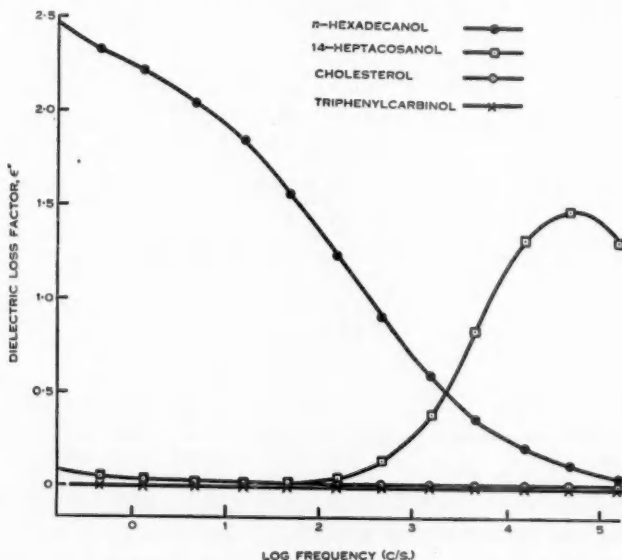


Fig. 2.—Effect of steric hindrance on dielectric absorption of alcohols.

some previous results for normal long-chain alcohols. It is seen that the two compounds with sterically hindered hydroxyl groups give comparatively small dielectric loss throughout the frequency range of measurement.

There is still the possibility of absorption at higher frequencies to be considered and in this connection it is useful to compare the low frequency values of the dielectric constant with those of long-chain alcohols of similar molecular weight. This comparison is given in Table 1.

It is evident from these results that although the dielectric constants of triphenylcarbinol and cholesterol are a little larger than the values expected from electronic and atomic polarization only, the amount of the enhancement is very small compared with that in the long-chain alcohols. Hence, any

absorption in triphenylcarbinol and cholesterol at higher frequencies must be small in comparison with the low frequency absorption in the alcohols.

TABLE 1
COMPARISON OF LOW FREQUENCY DIELECTRIC CONSTANTS

Compound	Formula	Relative Density	Dielectric Constant at 100 c/s.
Triphenylcarbinol	$C_{18}H_{16}O$	1.12	2.9
Cholesterol	$C_{27}H_{46}O$	1.01	2.5
10-Nonadecanol	$C_{18}H_{36}O$	0.91	21.0
14-Heptacosanol	$C_{27}H_{54}O$	0.91	17.0
Triphenylmethane	$C_{18}H_{16}$	—	2.45 (Lautsch 1928)
n-Hydrocarbons	—	0.95	2.25

The latter conclusion was further investigated by making some high frequency measurements of triphenylcarbinol and cholesterol. The results are given in Table 2. Both compounds show some dielectric loss at the highest frequency of measurement. It is possible that this loss is due to hindered rotation of the free hydroxyl group.

TABLE 2
DIELECTRIC LOSS IN TRIPHENYLCARBINOL AND CHOLESTEROL AT HIGH FREQUENCIES

Compound	Dielectric Loss Factor at:			
	10^6 (c/s.)	3×10^8 (c/s.)	8.6×10^8 (c/s.)	2.4×10^{10} (c/s.)
Triphenylcarbinol	≤ 0.001	≤ 0.001	0.007	0.011
Cholesterol	—	—	≤ 0.002	0.007

The small value of the dielectric loss in triphenylcarbinol and cholesterol compared with that in long-chain alcohols supports the theory that the abnormally large absorption in the latter is associated with hydrogen-bonding of the hydroxyl groups. In terms of this theory, the comparative absence of absorption in triphenylcarbinol and cholesterol can be explained as being due to the hindering effect of their molecular structures on the formation of hydrogen-bond chains.

(b) *tert.*-Butanol

The results for this compound in the crystalline state are compared in Figure 3 with those for *n*-octanol. This is the lowest molecular weight *n*-primary alcohol of the series previously investigated (Hamon and Meakins 1952).

The results show that although *tert.*-butanol gives some low frequency dielectric loss, it is considerably less than that for *n*-octanol at similar temperatures, despite the larger hydroxyl concentration of the former. It thus appears

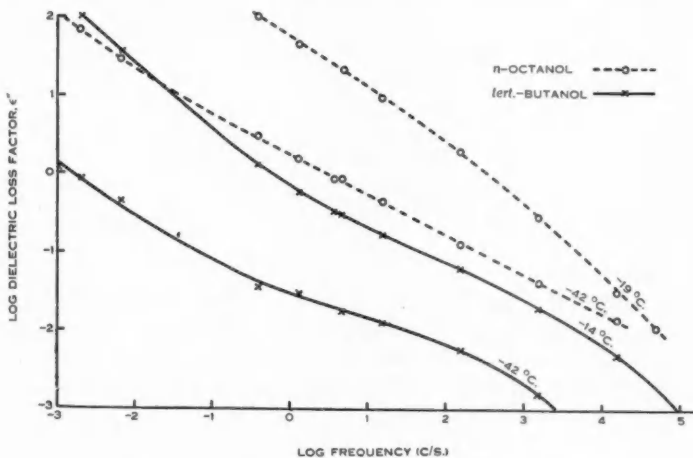


Fig. 3.—Dielectric absorption of *n*-octanol and *tert.*-butanol.

that hydrogen-bonding is present in crystalline *tert.*-butanol, but is of smaller extent than in *n*-primary alcohols. This is in agreement with the structural considerations in Section I.

V. ACKNOWLEDGMENTS

The author wishes to thank Dr. J. S. Dryden, Division of Electrotechnology, C.S.I.R.O., for help in the measurement of triphenylcarbinol at high frequencies and also Miss J. W. Mulley, Division of Industrial Chemistry, C.S.I.R.O., for making some of the low frequency measurements.

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STUDY OF ADSORPTION ON METALS BY THE CONTACT POTENTIAL TECHNIQUE

By J. R. ANDERSON* and A. E. ALEXANDER†

[Manuscript received October 22, 1952]

Summary

The change in contact potential between metals due to physical adsorption of water vapour, isopropanol, and ethyl acetate has been studied. The plot of contact potential against relative vapour pressure showed a hysteresis loop, the behaviour varying for different methods of surface preparation. An initial irreversible potential change was always found, due to chemisorption. By studying the dependence of the contact potential on the temperature of one of the metal surfaces it has been possible to determine the change in work function of a gold surface due to physical adsorption.

I. INTRODUCTION

Although the study of phase boundary potentials has been used considerably in the past to obtain information about films adsorbed at the air-water interface (cf. Adam 1941), the corresponding study of metal surfaces has received much less attention. This is due no doubt to the more difficult experimental techniques involved.

The measurement of contact potentials (C.P.) has been used to some extent in the study of chemisorption (Bosworth and Rideal 1937; Bosworth 1945) but very little with physical adsorption. Frost and Hurka (1940) studied the adsorption of ethyl acetate, chloroform, and benzene on a system consisting of two gold plates one of which was coated with paraffin or *p*-nitraniline to a thickness of 0.1–0.5 mm. Adsorption was accompanied by appreciable potential changes but these workers were not able to give a satisfactory interpretation of their results. The inherent difficulty is that the observed potential changes result from changes in the work functions of both surfaces since *a priori* adsorption must occur on both. The only available data for the changes in work function of a gold surface with the adsorption of gases and vapours come from the photoelectric threshold studies of Ouillet and Rideal (1935). They reported that light petroleum, benzene, chloroform, and carbon tetrachloride were without effect on the work function, but ethyl ether, ethanol, and acetone brought about reductions of about 490 meV.‡ They also found that oxidation of the gold surfaces produced a progressive increase in the work function.

Mignolet (1950) investigated the adsorption of nitrogen, hydrogen, ethylene, argon, and xenon on evaporated nickel films and claimed that in all cases physical

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‡ Throughout this paper meV. is used for millielectron volt.

adsorption produced potential changes due to the formation of a dipole layer oriented positive away from the metal. However, the published account of this work includes the statement "(Van der Waals) films on bare nickel are stable in vacuo, surface potential (change in contact potential) variations of about 5% being sometimes observed by pumping". It therefore seems very doubtful if these films studied by Mignolet were physically adsorbed at all. Similarly, the results of Dubois (1930) and Duhn (1943) which were obtained after exposure of outgassed metal surfaces to the gas or vapour in question followed by pumping to a hard vacuum quite definitely refer to chemisorption.

The present investigation was undertaken in order to study the effect of physical adsorption on the contact potential between metals, and to throw some light on both the nature of the metal surfaces and the adsorption processes involved. The metal surfaces used were gold, nickel, and copper and the materials adsorbed were *isopropanol*, water, and ethyl acetate.

II. EXPERIMENTAL

Contact potential measurements were made using the vibrating plate technique of Zisman (1932). The signal generated by the vibrating condenser was amplified and displayed on an oscilloscope. A null method of measurement was employed using a potentiometer in the side of the circuit near earth.

The first stage of amplification used a miniature electrometer tube (VX3094) with a grid resistance of 10^{10} ohms. This was done to make the input impedance and thus the conversion efficiency as high as possible (cf. Anderson and Alexander 1952). In order to eliminate microphonics the electrometer stage was mounted on sponge rubber and a filter circuit was incorporated. Due to the nature of the apparatus, the lead connecting the experimental cell to the electrometer stage had to be about 40 cm. long. No available type of commercial coaxial cable was satisfactory due both to the high shunting capacitance and to microphonics introduced by vibration in the cable itself. The only satisfactory arrangement was a specially constructed lead which consisted of a brass rod ($\frac{3}{16}$ in. diam.) rigidly supported centrally in a brass tube ($1\frac{1}{4}$ in. diam.) by polystyrene spacers.

The working cell containing the vibrating condenser is shown diagrammatically in Figure 1. The vacuum pump was a two-stage high-speed mechanical oil pump (protected by a cold trap) which could be used to evacuate the system to 1μ .

The frequency of the vibrating condenser was 45–46 c/s., the amplitude approximately 1 mm., with a minimum clearance between the plates of about 0.5 mm. A precision of ± 1 mV. was obtained. Measurements made at room temperature were in the range 21–24 °C.

For heating specimens in vacuum, the heater shown in Figure 2 was used. The heater leads were taken out through seals in the vacuum system.

In presenting the results, the convention is adopted that a positive change in potential is due to a positive excursion of the potential of the *bottom* plate. This is thus equivalent to a reduction in the work function of this surface or an increase in the work function of the top surface. A decrease in work function results

from the formation of a dipole layer oriented positive away from the surface. In all cases the top plate was gold. The bottom plate could be heated if desired.

The gas pressures were generally measured by using a mercury filled closed-end manometer, and reading the vertical heights with a cathetometer. The pressure readings are accurate to ± 0.05 mm. Hg. In a few runs a closed-end manometer filled with Dow Corning DC703 silicone diffusion pump oil was used. This manometer was not used extensively because the oil tended to absorb the

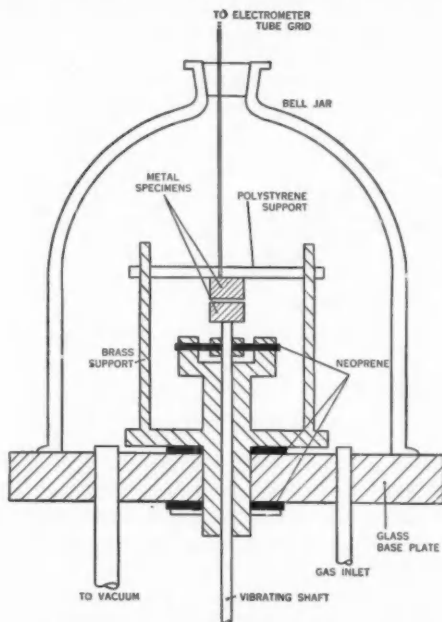


Fig. 1.—Apparatus for measurement of contact potentials.

organic vapour. No significant difference in the contact potential results was observed by the elimination of mercury vapour. All the glass taps in the vacuum and vapour handling system were greased with Dow Corning silicone high vacuum grease. In all cases the liquids were well outgassed by pumping before vapour was admitted to the cell.

The isopropanol and ethyl acetate were purified by careful fractionation of the commercially pure materials, the fractions boiling within 0.1°C . of the accepted boiling points being collected and used.

The electrodeposited gold, nickel, and copper surfaces were prepared by deposition on brass substrates from aqueous solutions of the following compositions per litre:

- (i) KCN 12.5 g.; $\text{KAu}(\text{CN})_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ 19 g.; KOH 12.5 g.; $\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ 6 g.

(ii) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 250 g.; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 37 g.; H_3BO_3 37 g.

(iii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 225 g.; H_2SO_4 37 g.

The metals were deposited to a thickness of about 0.002 cm., washed for several hours in running water, then in distilled water, and finally dried in a desiccator over silica gel. The electropolished nickel and copper surfaces were prepared from samples of the pure metals using the directions given by Kemsley and Tegart (1948). On removal from the polishing baths these specimens were washed and dried as described above. Attempts to prepare gold surfaces by electropolishing were unsuccessful since the specimens consisted of gold sheet hard soldered to a brass support and there was extremely rapid corrosion of the brass during the polishing process. This corrosion could not be prevented by plating with gold since the coating lifted off and the base metal was attacked

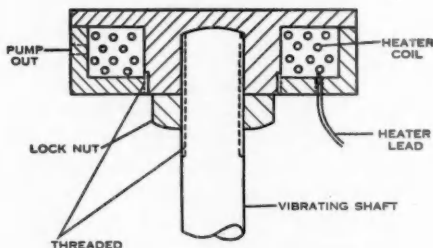


Fig. 2.—Design of heated electrode.

before any appreciable polishing had taken place. The gold surfaces (other than those prepared by electrodeposition) were prepared by a polishing process, finishing on heavy magnesium oxide, and etching to remove the amorphous layer for 1 min. at 60 °C. in a solution containing 15 per cent. KCN and 15 per cent. $(\text{NH}_4)_2\text{S}_2\text{O}_8$, followed by washing and drying as described above. In all cases, the surfaces as prepared would be covered with oxide films.

When the heated plate was used, it was not possible to measure the temperature and contact potential simultaneously, therefore the following procedure was adopted. In a separate experiment, temperature *v.* time curves were obtained for constant values of the heating current. The temperature measurements were made by means of a calibrated nickel-constantan thermocouple of 40 SWG. wire, the junction of which was placed in contact with the surface in question, good thermal contact being established by a small drop of high vacuum pump oil. The position of the thermocouple on the surfaces was varied and it was found that the temperature over the surface was constant to within 3 °C. Heating rates were determined under vacuum and also under various pressures in the range 5–25 mm.

III. RESULTS AND DISCUSSION

(a) Effect of Heating One Gold Plate

We must first consider whether the work function of a metal is intrinsically temperature dependent, since this will lead to changes in addition to those due

to the adsorption and desorption processes in which we are interested. The experimental evidence is very uncertain. However, for tungsten, the only metal for which any data are available, the temperature coefficient (α) is about 10^{-4} to 10^{-5} eV./deg. (Nottingham 1936; Fowler and Guggenheim 1949), when α is defined by

$$\chi = \chi_0(1 - \alpha T),$$

where χ is the work function. Using these data a temperature rise of 100 °C. would result in a decrease in χ of about 4–40 meV. There are, however, no

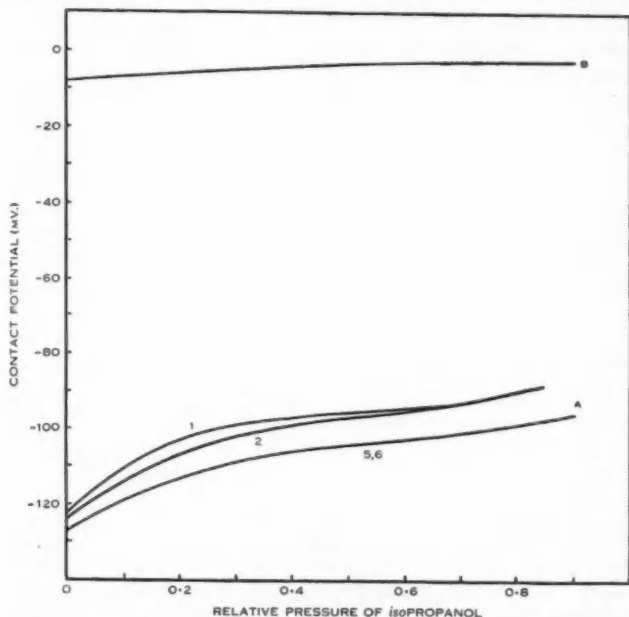


Fig. 3.—Adsorption of isopropanol on two electrodeposited gold surfaces. A, one surface fresh; one surface after repeated heating. B, both surfaces after repeated heating.

data for any other metal and this correction will henceforth be neglected, bearing in mind that it is in any case probably small but may still be significant.

Experiments were conducted (using two electrodeposited gold surfaces) which showed how heating (followed by cooling) of one surface may affect the potential change due to subsequent adsorption of alcohol vapour. One surface (the top plate) had been used about 12 times to study the adsorption of isopropanol and between runs had been heated under vacuum to about 150 °C. The bottom gold surface was freshly prepared. Before the first run both surfaces were heated to about 150 °C. under vacuum and cooled under vacuum. Subsequent adsorption of isopropanol gave results which are plotted in Figure 3. It

will be seen that even though the overall potential change was largest for the first two series and then decreased slightly, the potential change going from vacuum to a relative pressure of 0.95 was still appreciable after the 6th run—about 30 mV. The bottom plate was now demounted, heated to 150 °C., and cooled under vacuum four times, being exposed to *isopropanol* immediately prior to heating. The adsorption of *isopropanol* now gave results which are also shown in Figure 3, curve *B*. It is evident that the two surfaces had now become very similar, the adsorption of alcohol only producing an overall potential change of +6 mV. Moreover, the absolute magnitude of the C.P. was now close to zero.

The effect of heating the bottom plate under vacuum and in *isopropanol* and in water vapour was investigated. In these experiments both plates consisted of a piece of gold sheet about 0.5 mm. in thickness silver-soldered to a brass supporting plate. The surface of each plate was prepared by polishing as described previously. Two values of heating current were used, namely, 0.6 and 1.5 A. The top plate was heated by radiation and convection, the rate being largely dependent on the gas pressure. Correction for this was made so as to obtain the potential changes due to the temperature rise of the bottom plate only. This was done by a method of successive approximation using the initial portions of the 0.6 A. curve as references, since in this case the temperature increment of the top plate was negligible. This method of correction assumes that the two surfaces were at this stage identical. Although this is not accurately true, the error introduced should not be large since the temperature rise of the top plate was never more than c. 20 °C.

The original potential in vacuum varied over a range ± 50 mV. with no apparent order. Therefore, for recording results, the starting potential in vacuum is arbitrarily called zero and changes in C.P. from this zero are given. For each system a number of series was run.

(i) *Heating under Vacuum*.—A typical result for heating at 1.5 A. under vacuum is contained in Figure 4. It will be seen that the curve flattens off after a temperature increment of about 80 °C. The tendency to dip down again may be due to inaccuracy in correction for top plate heating. The magnitude of the overall potential change varied somewhat from one series to another but was in the range 60–150 mV. This change is probably due to the desorption of oxygen (and perhaps nitrogen). With one plate heated, the admission of air to about 100 mm. pressure resulted in an immediate change in potential of -42 mV. which is ascribed to physical adsorption on the unheated plate, since this change was reversible on pumping down.

The change in C.P. due to heating is not very strongly dependent on the air pressure with which the surfaces were in contact, at least over the range 1 μ to 100 mm. Increasing the pressure over this range increased the change in C.P. by 40–50 mV. This result was obtained by direct experiment and was confirmed by the results given above in which the change in C.P. due to adsorption on the top unheated plate was measured. As the heating-cooling cycle was repeated the starting potential for each cycle progressively shifted to more negative

potentials, the shift being about 30–40 mV. per cycle for the first 3 or 4 cycles, after which no further shift was observed. Benton and Elgin (1927) showed that on heating, oxygen is chemisorbed by gold and the electron diffraction results of Moody (personal communication, 1951) show that moderate heating of gold in air leads to the presence of a surface oxide layer. This is probably the

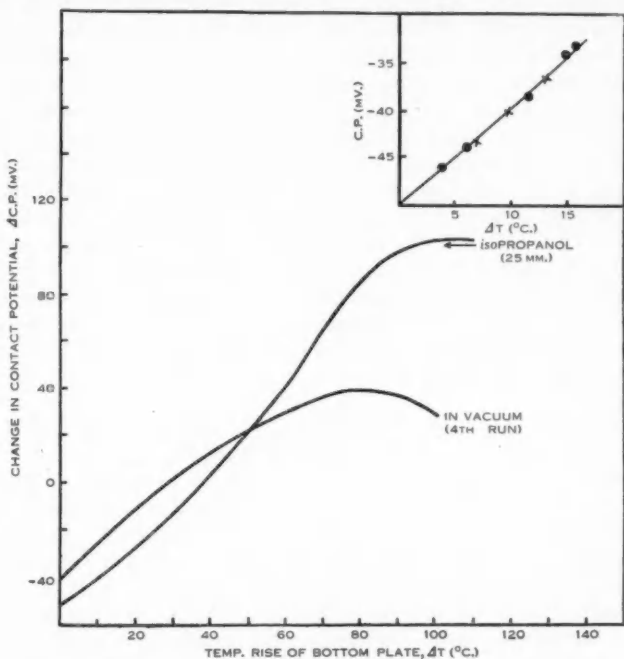


Fig. 4.—Contact potential change *v.* temperature rise of bottom plate. Potential at start of first vacuum run taken as zero. Heating curves at 1.5 A. Both surfaces of gold. Corrected for heating of top plate.

Inset: Results for 0.6 A. heating current.

- Heating.
- ×—×—×— Cooling.

reason for the progressive negative potential change caused by repeated heating of the gold electrode. This is in agreement with the results of Ouillet and Rideal (1935).

(ii) *Heating in isoPropanol and in Water Vapour.*—In each experiment, after the curves for heating under vacuum were obtained, *isopropanol* or *water vapour* was introduced and the temperature *v.* C.P. curves redetermined. The introduction of the vapour to the cold system was accompanied by a negative potential shift of about 10–40 mV. which shows that the two plates at this stage were not completely identical. This difference probably arose from the heating

to which the bottom plate had been subjected. Figure 4 shows a typical set of results obtained with *isopropanol* vapour. Water vapour gave similar results. The desorption of *isopropanol* or water from the gold surface results in an extra positive potential change of the order of 50–100 mV. superimposed on that which occurs under vacuum. Because of the variability of the values from system to system it did not seem feasible to try to obtain comparative figures for different vapour pressures. Most of the experiments in the presence of vapour were done at 23 mm. for *isopropanol* and 15 mm. for water vapour. A few runs were done with *isopropanol* at 1.2 mm. pressure, but no significant difference was found.

Only the heating curves are shown in Figure 4. In all cases with heating currents of 1.5 A. the corresponding cooling curves lie below the heating curves, the tendency being most pronounced with the system in vacuum. The reason for this is thought to be that the initial regions of the heating and cooling curves do not represent equilibrium potential values, since in this region the rate of temperature change was very large. However, the systems are considered to be in equilibrium at higher temperatures on the heating curve, since here the rate of heating was slow. For instance, the time taken for the temperature to rise from 90 to 110 °C. was 23 min. In the case of 0.6 A. where the initial rates of heating and cooling were slower, the heating and cooling branches coincide as shown in the inset to Figure 4.

The sign and magnitude of the potential change due to the desorption of *isopropanol* and water vapour by heating shows that the adsorption of these vapours on to a gold surface causes an increase in the work function of the gold by about 50–100 meV. This would be due to the formation of a dipole layer on the gold oriented negative away from the metal surface. This is in the opposite direction to that claimed by Ouillet and Rideal (1935) for ethanol from photoelectric threshold studies. The contact potential method does not, however, suffer from the uncertainty in the extrapolation used to locate the threshold. As pointed out by Fowler and Guggenheim (1949), any method of finding the threshold which does not involve a study of the temperature dependence of the photoelectric yield is liable to be quite unreliable.

The direction of dipole orientation of *isopropanol* on gold is opposite to that observed for alcohols adsorbed at the air-water interface (cf. Adam 1941). The magnitude of the potential change due to adsorption on a gold surface is quite small compared with the change in phase boundary potential produced by adsorption at the air-water interface, where even relatively dilute adsorbed films of aliphatic alcohols produce potential changes of up to 400 mV. (cf. Posner, Anderson, and Alexander 1952).

The recent work of Bowden and Throssel (1951) would indicate that, under the present experimental conditions, the thickness of the adsorbed layer would be more than monomolecular over most of the experimental pressure range. Yet it was found that the change in work function was comparatively small—in the range 50–100 meV. This seems to indicate that if the adsorbate is present as a multilayer, there is either no high degree of orientation in the successive layers or, if such orientation is present, the dipoles in each layer are oppositely

oriented so that the overall potential change is small. At room temperature where $RT \approx 600$ cal./mole and is quite appreciable compared with intermolecular forces between the small molecules studied, it seems probable that the degree of orientation would not be high, at least no greater than in the bulk liquid.

(b) *Differential Adsorption using Gold/Nickel and Gold/Copper Pairs*

An attempt was made to measure the potential change due to adsorption of water vapour on one gold surface by rendering the other gold surface hydrophobic by coating it with silicone or palmitic acid. Although potential changes

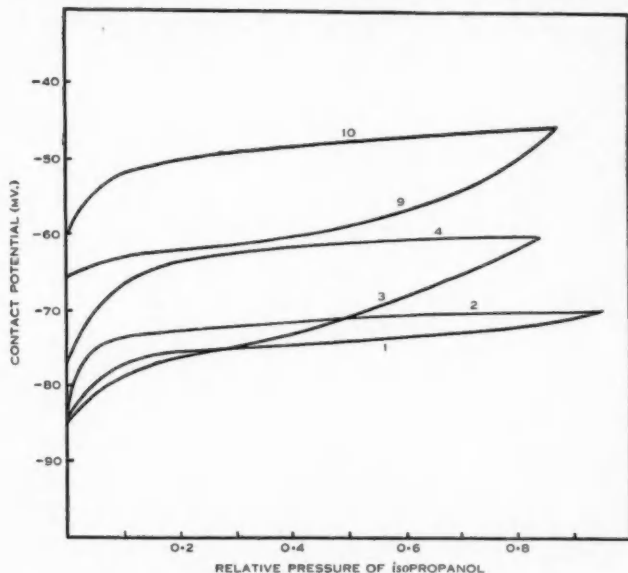


Fig. 5.—Adsorption of isopropanol on electrodeposited nickel/gold.

were obtained, the results were not sufficiently reproducible for any conclusions to be drawn.

In the experiments described in subsequent sections, the metal specimens, before use, were heated to 150°C . under vacuum ($<10^{-4}$ mm.) for 5 min. (in a separate apparatus) and cooled under vacuum before mounting for measurement. The initial potentials under vacuum were rather variable and for both the gold/nickel and gold/copper systems were in the range -100 to -200 mV.

(i) *Gold/Nickel*.—Representative results obtained with electrodeposited nickel for the adsorption of isopropanol are shown in Figure 5. Increasing alcohol pressure was accompanied by a positive potential change. As will be seen from the results, hysteresis was marked over the whole pressure range. As far as it is possible to judge, this hysteresis was not caused by non-equilibrium conditions since at each point the potential was allowed to come to apparent

constancy with time, this process taking generally 10–15 min., particularly in the regions of very low and very high relative pressures. Where there was any appreciable change in potential with time, the value plotted was obtained by graphical extrapolation. Even so, the correction due to extrapolation amounted in the worst case to only 5 mV. From Figure 5, it is clear that in addition to marked hysteresis there was a progressive shift towards more positive potentials, this drift still being evident after the tenth run. Qualitatively similar results were obtained with water and ethyl acetate. The electrodeposited nickel

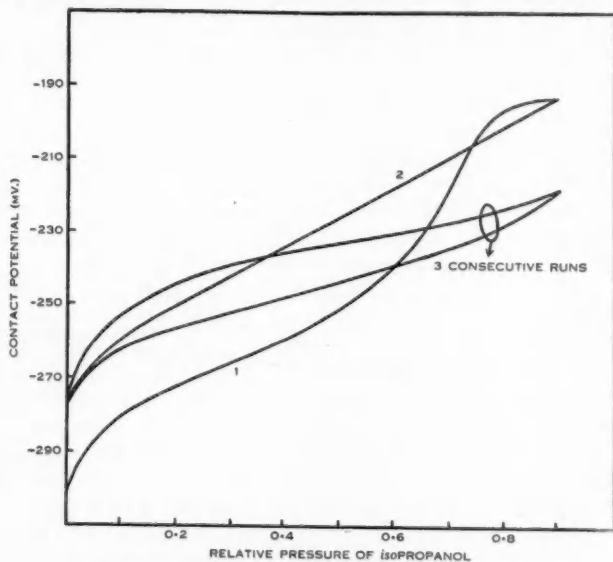


Fig. 6.—Adsorption of isopropanol on electropolished nickel/gold.

surfaces were, of course, unpolished and appeared to have a dull, mat finish when viewed by the unaided eye.

Typical results for electropolished nickel are shown in Figure 6 for isopropanol. It will be seen that the first run with isopropanol gave a large irreversible potential change. An irreversible change of a similar type was also found with the fresh electrodeposited surfaces. Subsequent runs on the electropolished surfaces were, however, quite reproducible and in contradistinction to the results for electrodeposited nickel there was no tendency for the potential to drift. The hysteresis loop is still present but is very much reduced in size. Again, the presence of this loop does not appear to be a function of non-equilibrium conditions. Qualitatively similar results were obtained with water and ethyl acetate.

(ii) *Gold/Copper*.—For electrodeposited copper, the results resemble those for nickel except that with copper, the initial irreversible potential change was

present to a greater degree than with nickel. The behaviour of electrodeposited copper surfaces with regard to hysteresis varied according to the nature of the surface. A rough and perhaps more porous layer gave marked hysteresis, but a smooth layer gave somewhat smaller hysteresis. Unfortunately, the results for electropolished copper are complicated by variation in the sign of the potential change from sample to sample, due apparently to uncontrollable differences in the surface preparations. This may be due to the presence of a phosphate layer (from the polishing electrolyte). The use of a wash in 10 per cent. aqueous phosphoric acid to produce a phosphate-free surface, as recommended by Jacquet and Jean (1950), did not, however, effect a cure. On electropolished copper surfaces, hysteresis was still present but only to a small degree. An irreversible potential change was again found with the first adsorption run.

The magnitudes of the potential changes due to adsorption on the gold/nickel and gold/copper pairs are comparatively small (except for the initial irreversible changes) and this reflects the non-specificity of physical adsorption on the two metals of each pair. Such non-specificity is to be expected for physical adsorption since it is not dependent on any specific chemical interaction.

Assuming that adsorption alters the work functions of the metals of each pair in the same direction, it may be concluded from the sign of the potential changes that the change in work function is smaller for gold than for either of the other metals. In the absence of any additional information it would be unwise, however, to conclude from this that adsorption was necessarily least on the gold surfaces. The initial irreversible potential changes are probably due to chemisorption. It was also found (see later section) that a similar irreversible change was produced by the treatment of a freshly abraded copper surface with water vapour.

The presence of a repeatable hysteresis loop on an electropolished surface appears at first surprising. The work of Rhodin (1950) shows that hysteresis does not occur in the low temperature physical adsorption of nitrogen on electropolished single crystals of copper (which by extremely careful preparation had a roughness factor as low as 1.2). However, adsorption hysteresis has been found to occur with more complex molecules on plane surfaces and on non-porous adsorbents. Bangham and Mosallam (1938) found hysteresis over the whole pressure range in the adsorption of benzene on cleaved mica surfaces and Pierce and Smith (1950) extensive hysteresis in the adsorption of water on a non-porous carbon. This type of hysteresis appears to differ from that due to capillary condensation on porous adsorbents since in the latter case the hysteresis loop is generally limited to the region of higher relative pressures.

Explanations of hysteresis of this type, based on a cooperative effect in the adsorbate, have been advanced by Hill (1947) and by Pierce and Smith (1950). The possibility that increasing adsorption is accompanied by a change in average orientation of adsorbed molecules was suggested by Bangham and Mosallam (1938) and it seems that this process would also be admissible in the theories of Hill (1947) and of Pierce and Smith (1950). However, that such an orientation change may itself exhibit a hysteresis effect without *any* corresponding hysteresis

in the total amount adsorbed seems rather unlikely. A similar process may, of course, also occur on electrodeposited surfaces; however, here the situation is more complex. It seems significant that the most pronounced hysteresis which occurred with electrodeposited surfaces, was accompanied by an overall potential shift. This may be due to the slow displacement of oxygen from the surface which would give a shift in the observed direction.

(iii) *Gold/Abraded Copper*.—The copper specimens were machined from commercial grade bar.* The gold specimen consisted of $\frac{1}{32}$ in. pure gold sheet, hard soldered to a brass support. Both surfaces were prepared by abrading dry on 600 grade "Hydrodurexsil" paper and then mounted immediately in the apparatus.

Heating the copper surfaces under vacuum to 150 °C. for 30 min. and cooling to room temperature resulted in a shift of about -200 mV. This heating was no doubt accompanied by a slight increase in the thickness of the oxide film due to oxidation by the residual gas. However, it seems unlikely that this will have any marked effect on the work function of the copper since the original surface was already covered with an oxide layer of considerable thickness. We therefore attribute this potential change to a structural alteration in the film immediately in contact with the copper. There is the possibility that heating results in a certain amount of recrystallization or some change of structure of the surface layer of copper which was deformed during abrasion. Although this would result in some change in the work function of the surface, it seems doubtful if the temperatures used would be sufficient for this process to occur to a significant extent. The most likely explanation appears to be an increase in the proportion of CuO in the oxide film which originally consisted almost entirely of Cu₂O. This is supported by the observations of Cruzan and Miley (1940) who found that in oxide films produced on copper by heating in air at 240 °C., the CuO content increased with the period of heating.

Results for the adsorption at room temperature of water vapour at a constant relative pressure of 0.84 are shown in Figure 7. The results were the same using a copper specimen which had been heated to 150 °C. for 30 min. under vacuum. The large positive potential change shown in Figure 7 was irreversible and pumping down and subsequent re-admission of water vapour caused only a smaller reversible change of 30–40 mV. positive with increasing pressure, superimposed on the irreversible change. The magnitude of this irreversible change varied from specimen to specimen in the range 100 to 250 mV. depending presumably on the exact nature of the oxide surface prior to the experiment. The initial portion of the curve in Figure 7 is shown dotted since this region is indefinite owing to the finite time taken for the relative pressure of the water vapour to reach 0.84. After reaching equilibrium at room temperature subsequent heating of the copper specimen to 150 °C. for 10 min. in water vapour (at a relative pressure of 0.84) followed by cooling to room temperature produced no further appreciable change in potential. Because of the inert nature of gold it is considered that the irreversible change caused by water vapour is due to

* Composition: Copper not less than 99.85 per cent.; oxygen not more than 0.1 per cent.

some chemical change occurring at the copper oxide surface. Cuprous hydroxide has not been isolated as a chemical identity, so one should be wary of postulating the formation of cuprous hydroxide on an oxide surface. Nevertheless conditions in the surface may be sufficiently different from the bulk for this to be possible. The fact that as far as one can tell from contact potential measurements the effect of water vapour on a copper oxide surface goes to completion at room temperature makes an interesting comparison with the

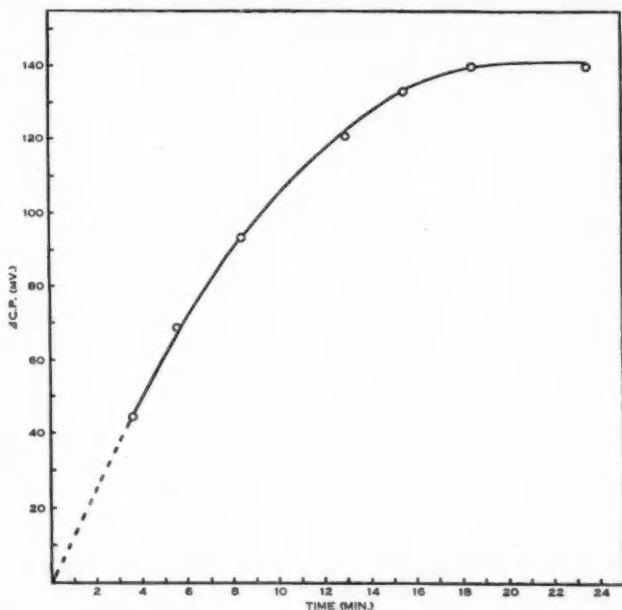


Fig. 7.—Irreversible change in contact potential between abraded copper and gold due to water vapour.

results of Tingle (1950) who found that it was necessary to treat an oxide covered copper surface with boiling water in order to obtain the most effective lubrication of the surface with lauric acid. A suggestion of Tingle that treatment with boiling water leads to the formation of a thicker and more porous oxide or hydroxide film (which then allows a thicker lubricating layer to be formed) would be consistent with the present results if an increase in thickness causes no appreciable change in potential.

IV. ACKNOWLEDGMENTS

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STUDIES OF AGGREGATION IN SOAP SOLUTIONS CONTAINING SALT AND SIMPLE ORGANIC MOLECULES

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Summary

Using the synthetic soap cetyl pyridinium chloride the effects of added chlorobenzene and sodium chloride upon various physical properties, such as saturation solubilities, viscosity, osmotic pressure, sedimentation velocity, and interfacial tension, have been quantitatively measured. The results suggest that the soap micelle has a very labile structure, the approximately spherical aggregates present in pure soap solutions changing to more asymmetric shapes in the presence of suitable concentrations of sodium chloride and chlorobenzene.

I. INTRODUCTION

There is now general agreement that, in dilute aqueous soap solutions, only one type of micelle exists—the approximately spherical, ionic micelle suggested by Hartley (1936). Uncertainty still persists, however, regarding the size and shape of micelles in the more concentrated solutions and the conclusions to be drawn from the effects of salts and organic additives upon both dilute and concentrated soap solutions.

In the absence of simple electrolytes it has often been suggested that strong soap solutions contain laminar or cylindrical aggregates (for references see Alexander and Johnson 1949). The X-ray diffraction patterns of such solutions formed the main basis for these conclusions, but more recently Corrin (1948), Hartley (1949), Philipoff (1950), and Winsor (1952) have advanced alternative explanations. Hartley assumes a tetrahedral arrangement of charged spheres which yields values of the radius in good agreement with those found by other means (for example, diffusion) in dilute solution. Philipoff and Winsor differ somewhat from Hartley as will be discussed in more detail later.

Support for the existence of spherical micelles in the more concentrated solutions comes from the work of Hartley (1938) upon the solubility of *trans*-azobenzene in aqueous solutions of cetyl pyridinium chloride (hereafter written as C.P.Cl). His results have been replotted—in rather a different manner from that given in the original paper—as Figure 1, the dotted line indicating the solubility obtained by extrapolation from concentrations just above the micellar-point (that is, over the range 0.001 to 0.004M). Below 0.1M the molecular ratio of azobenzene to soap has a constant value of 0.17. Between 0.1 and 0.5M this ratio increases slightly, the value at 0.5M being 0.23. If, as the

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exponents of the laminar micelle have suggested, the non-polar organic molecules are held between the layers of hydrocarbon tails, the molecular ratio would be expected to increase quite markedly with the soap concentration. Figure 1 however, clearly indicates that, at least up to 17 per cent. solutions (*c.* 0.5M), the micellar change in shape cannot be very great. Because of micelle-micelle interaction, which will increase with the soap concentration, some deviation from

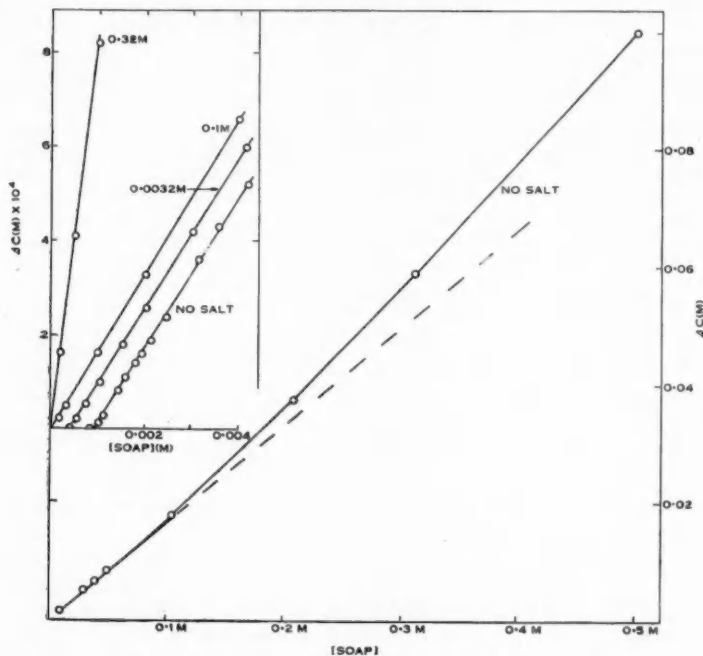


Fig. 1.—The solubility of *trans*-azobenzene in aqueous solutions of cetyl pyridinium chloride.

Inset: The solubility in the presence of various concentrations of sodium chloride. $\Delta C(M)$ = molar concentration in soap solution minus molar concentration in water. (Replotted from the data of Hartley (1938).)

a spherical shape is to be expected, and this would provide a reasonable explanation for the small increase in the solubility coefficient.

The effect of salts on the size of micelles in dilute aqueous solutions of a few cationic soaps (mainly alkyl trimethylammonium bromides) has been investigated by Debye (1949) using the technique of light-scattering. He finds that the size of the micelles is significantly increased by very small additions of salts, and that the micelle-weight increases with increasing salt concentration. The highest salt concentration used was 0.046M. Hartley and Runnicles (1938), however, using the method of diffusion through a porous disk, have shown that the size

of the C.P.Cl micelle is approximately constant over a 25-fold range of soap concentration (0.002–0.05M) and over the range of salt concentration from 0.04 to 1.0M. Confirmation of Hartley and Runnicles's results is reported by Bevilacqua *et al.* (1945) and by Miller and Andersson (1942).

A change in the size or shape of the micelle on the addition of salt might be expected to be reflected in the solvent-power of the soap for non-polar organic molecules. Many investigations in connection with this aspect are to be found in the literature (for review see Klevens 1950), but most of the work has been done either at only one concentration (usually 0.1M) or with the fatty acid soaps, and in both cases the interpretation of the results is not easy. Hartley (1938) on the other hand has measured the solubility of *trans*-azobenzene in solutions of several cetyl pyridinium salts (chloride, bromide, sulphate, acetate) in the presence of the corresponding sodium salts, over a range of both soap and salt concentration. Some of his results are replotted as an inset to Figure 1, from which it is clear that, when the salt concentration is less than 0.1M, the molecular ratio is 0.17, the value found in the absence of any salt. However, when the solutions are 0.32M with respect to salt, the molecular ratio has risen to 0.82, which would seem to indicate some change in the shape or size of the micelles. The present investigation is mainly concerned with much higher soap concentrations than used by previous investigators and with a wider range of NaCl concentrations (up to 1M). Viscosities, saturation solubilities of chlorobenzene, osmotic pressure, interfacial tensions, and sedimentation velocities have been measured. Chlorobenzene was chosen because of its small size, very slight solubility in water, ease of purification, density, and insensitivity to light.

II. MATERIALS

The cetyl pyridinium chloride was a pure sample kindly given by W. S. Merrell Co. of Cincinnati. Fifteen per cent. solutions of the soap were colourless. Titration against pure sodium hexadecyl sulphate, using pinacyanol bromide as adsorption indicator (Salton and Alexander 1949), showed it to be 100 (± 0.5) per cent. C.P.Cl. The sodium chloride used was of A.R. quality and the chlorobenzene was redistilled just before use.

III. EXPERIMENTAL

(a) Determination of Saturation Solubilities

Since chlorobenzene has a higher density than any of the soap/salt solutions it was convenient to determine saturation solubilities by shaking an excess with the appropriate soap/salt mixture in a sealed Pyrex tube, the lower portion of which had been drawn to a fine, approximately constant bore of c. 1 mm. The tubes were maintained at $25.0 \pm 0.1^\circ\text{C}$. in a water-thermostat until the length of the chlorobenzene column in the narrower lower limb was constant after repeated shaking. The narrow limb was then broken off, cleaned, dried, and pure chlorobenzene added to form a column of exactly the same length. This volume was measured accurately by means of an Agla micrometer syringe, previously calibrated by weighing volumes of distilled water.

In strong salt solutions no separation of excess chlorobenzene occurred, even after several days, but a very stable emulsion was formed. The saturation solubility in these instances was taken as the concentration at which visible emulsification occurred, this being extremely reproducible when approached either from an excess of chlorobenzene or from an excess of the soap/salt mixture.

(b) *Viscosity Measurements*

The viscosities of simple soap/salt mixtures were determined in an Ostwald viscometer which conformed to B.S.S. 188/1937. It was necessary to work at 32.0 °C. in order to keep the soap in solution when high salt concentrations were present. The time of flow for water was 122 sec. Kinetic energy corrections have not been made, and the density of each soap/salt mixture was taken as equal to that of the corresponding salt solution.

With soap/salt/chlorobenzene mixtures the viscosities were frequently so high as to make a change in procedure necessary; they were accordingly measured by timing the flow of the solution between two graduation marks on a 1 ml. grade B pipette. A calibration curve was obtained from the times of flow of Newtonian fluids of known viscosity (for example, water, ethanol, "Nujol", castor oil). The soap/salt/chlorobenzene mixtures were non-Newtonian as the time of flow was very dependent upon the rate at which the solution was drawn up the pipette, but there was no discernible yield value: small, entrapped air-bubbles always rose steadily to the surface. Values of η cannot be widely in error, especially when η is large, as the rate of shear was very low.

(c) *Osmotic Pressure Measurements*

The literature appears to contain no reference to osmotic pressure studies of soap solutions. As with the proteins, true osmotic pressures can be obtained only when there is sufficient salt present to reduce the Donnan membrane effect to negligible values. A collodion thimble, attached by pressure-tubing to a length of glass capillary, formed the osmometer. The preparation of suitable membranes (that is, membranes through which single soap ions would not diffuse) was not an easy task, but was possible if Adair's procedure (see Alexander and Johnson 1949, Appendix 2) was followed but much thicker membranes were made. It was found that no two membranes gave the same osmotic pressure for a given soap/salt solution until they had been used a few times.

(d) *Sedimentation Velocity Studies*

The sedimentation constant, S , was measured for two soap/salt/toluene mixtures using an air-driven ultracentrifuge at *c.* 300,000 g.

(e) *Interfacial Tension Measurements*

A simple drop-volume technique was employed, the corrections of Harkins and Brown (1919) being applied.

IV. RESULTS AND DISCUSSION

Consideration of the present results in the light of other physico-chemical properties of soap solutions and of the factors believed to be important in causing

aggregation (Stainsby and Alexander 1950), leads us to the conclusion that soap micelles are comparatively labile structures, and that, depending upon the conditions (for example, soap concentration, salt concentration, concentration of organic additives), we may have a continuous range from the (approximately) spherical aggregate to long flexible rods and possibly even to plate-like structures. Definite equilibria between fixed structures (for example, spheres and rods), as postulated recently by several workers (Philipoff 1951; Winsor 1952) imply a definite organization of the hydrocarbon parts of the molecules which is certainly not in agreement with the conclusions from surface studies.

(a) *The System Soap/Salt*

The relative increase in viscosity* η_s , varies with the salt concentration as shown in Figure 2. C.P.Cl micelles are strongly charged particles and therefore the addition of salt should reduce η_s , the value becoming constant once electroviscous effects become negligible. This was observed with the 4 per cent. (0.118M) solution, but with the 15 per cent. (0.44M) solution η_s showed a minimum at c. 0.4M NaCl, then rising rapidly at the higher salt concentrations.

Since under the conditions used there was no question of the systems being thermodynamically unstable, the upswing can only be interpreted on the basis of increasingly asymmetric aggregates. Some indication of the shape is possible by comparing the above results with those for proteins of known axial ratio and having comparable sizes. Viscosity-concentration curves of haemoglobin and serum albumen in 2M NaCl solutions (Gutfreund, personal communication) are convenient for this purpose. The axial ratio of the serum albumen used, from sedimentation and diffusion studies, was 4.0, and η_s for a 15 per cent. solution was found to be 1.24. The aggregates in the 15 per cent. solution of C.P.Cl containing 0.8M NaCl would therefore have an axial ratio of about 4. Haemoglobin is much less asymmetric, with an axial ratio of 1.7; a 15 per cent. solution gave η_s as 0.76. Accordingly it would seem that, at the minimum of the upper curve in Figure 2, where η_s has the value 0.89, the soap aggregates are not spherical but on the average are somewhat distorted.

The above conclusion is supported by a calculation of η_s for a set of uncharged spheres. The following equation, which has been shown (Vand 1945) to give good agreement with experimental values for concentrated suspensions of glass spheres in a suitable liquid medium, may be used:

$$\eta_s = 2.5c + 4.2c^2 + 6.3c^3 + \dots, \dots\dots\dots (1)$$

where c is the volume-fraction of the solute; η_s (calc.) is then 0.62, which is considerably less than the value for the soap solution (0.89) and for the solution of haemoglobin ($\eta_s = 0.76$) with its known axial ratio of 1.7.

Another equation often used to predict the viscosity of concentrated solutions of uncharged spheres is the extension (Guth and Simha 1936) of the simple Einstein equation, giving

$$\eta_s = 2.5c + 14.1c^2. \dots\dots\dots (2)$$

* Name recommended by the Joint Committee of Rheology to replace "specific viscosity" as the dimensions are not those of a viscosity. Proceedings International Congress on Rheology, Holland, 1948, Sect. V. p. 66. (North Holland Publ. Co.: Amsterdam.)

When $c=0.15$, $\eta_s=0.69$, in fair agreement with that calculated above from equation (1).

The alternative explanation, that the discrepancy between the observed and calculated viscosity is due to hydration (Philipoff 1951) can be ruled out since a soap micelle should differ little from a protein molecule in this respect, and the upswing in Figure 2 would be quite inexplicable.

The osmotic pressure determinations of micellar size (being an equilibrium method the shape factor does not enter) are shown in Table 1. No consistent values were obtained for salt concentrations below 0.17M even though, from the viscosity data, much lower salt concentrations were sufficient to swamp any charge effects in solution.

TABLE 1
THE SIZE OF C.P.Cl AGGREGATES IN SALT SOLUTIONS, DETERMINED FROM OSMOTIC PRESSURE MEASUREMENTS

Soap Concentration (M)	Salt Concentration (M)	Osmotic Pressure* (cm. water)	Number of Soap Molecules per Micelle†
0.118	0.17	67	41
0.118	0.34	65	42
0.118	0.68	80	34
0.05	0.5	32.6	36
0.03	0.17	14.0	48
0.03	0.34	18.0	38

* Values of the osmotic pressure have been corrected for capillary rise.

† Calculated assuming the partial molar volume of the solvent to be equal to 0.018 l., independent of the salt concentration.

It is clear from these results that, even in a 4 per cent. (0.118M) C.P.Cl solution, the aggregates cannot be very asymmetric, for a sphere of radius 22 Å would be expected to contain about 50 molecules.

(b) The System Soap/Salt/Chlorobenzene

The two phenomena which have been extensively studied, and for which some interpretation is necessary, are the striking changes in the viscosity and in the solubility of chlorobenzene. It was unfortunately impossible to obtain any osmotic pressure results with these systems. Membranes which required a week to reach equilibrium in the absence of chlorobenzene allowed soap/salt/chlorobenzene solutions to leak through in a few hours. Hartley and Runnicles (1938) encountered a similar difficulty when attempting to measure the diffusion coefficient of such solutions by means of a porous disk method.

(i) *Sedimentation Velocity Results.*—The following results were obtained at 20 °C.: Solution 1: 0.016 ml. toluene per 5 ml. soap/salt solution. (This small amount of toluene served to keep the soap in solution at room temperature.)

$$10^{13}S = 2.35 \pm 0.1; \quad r \approx 21 \text{ \AA} \quad (\text{see below}).$$

Solution 2: 0.159 ml. toluene per 5 ml. soap/salt solution. (System almost saturated with toluene.)

$$10^{13}S = 3.3 \pm 0.1; \quad r \approx 28 \text{ \AA} \quad (\text{see below}).$$

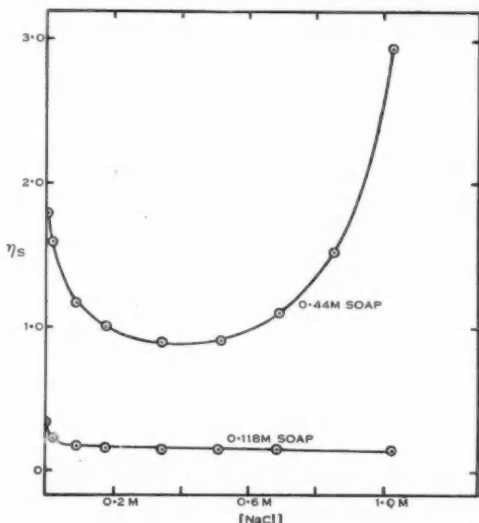


Fig. 2.—The effect of sodium chloride upon the relative increase in viscosity (η_s) of cetyl pyridinium chloride solutions (0.44 and 0.118M).

Both solutions contained 0.118M soap and 0.68M salt, both had the same viscosity (equal to that in the absence of toluene), and both sedimented *upwards*, that is, the partial specific volume \bar{V} , must have been greater than unity. In order to calculate the radius (r) of spherical aggregates having the observed values of S it was assumed that the density of the mixed aggregate was determined solely by the relative proportions of soap and toluene present.

(ii) *Viscosity Phenomena.*—Addition of chlorobenzene to aqueous soap/salt solutions produces considerable viscosity changes, as shown by Figure 3 for the system C.P.Cl/NaCl. This phenomenon has been noted previously (Hartley 1938), and in the case of the fatty acid soaps/phenols systems has been extensively studied by Angelescu and his co-workers (1941). The effect is a general one, as we have found that it is induced by such compounds as toluene, *n*-octane, and *p*-dichlorobenzene with both anionic and cationic soaps, and that it is quite reversible with respect to temperature and to the concentration of the organic

compound. In the absence of salt only small viscosity changes occur, and then only in strong solutions (0.3–0.5M C.P.Cl).

The very viscous solutions when flowing in a test tube display marked streaming birefringence, indicating the presence of very asymmetric aggregates. The less viscous solutions showed no birefringence under similar conditions but this may have been due to the low rate of shear.

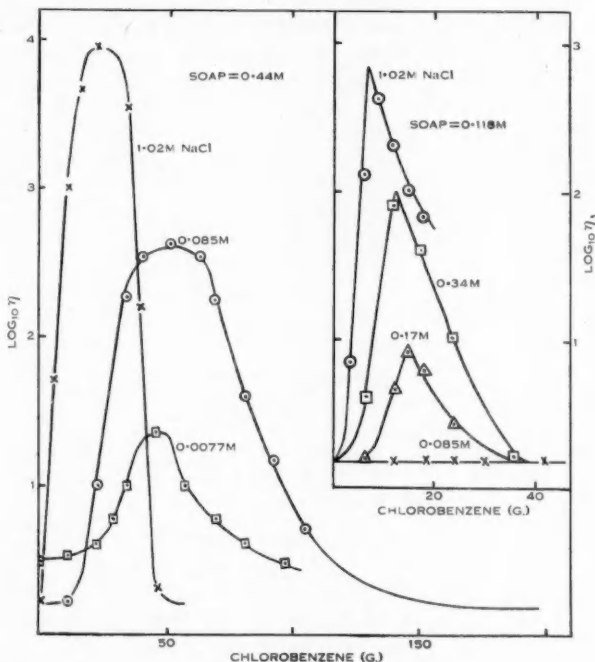


Fig. 3.—The effect of chlorobenzene upon the viscosity of cetyl pyridinium chloride/sodium chloride mixtures.

The more dilute soap solutions became bluish in colour on the addition of chlorobenzene, indicating that quite large aggregates were present (at least 1000 Å in one dimension).

(iii) *Interfacial Tension Results.*—Measurements of the interfacial tension (I.T.) of 0.367M soap solutions saturated with chlorobenzene, against pure chlorobenzene, gave the following values at 25.0 °C.:

No salt present: I.T.=1.42 dyn./cm.,

0.17M salt present: I.T.=0.71 dyn./cm.

(Against water, chlorobenzene has an I.T. of 33 dyn./cm. at 25 °C.; against 0.17M NaCl 35 dyn./cm.) At higher salt concentrations the I.T. falls even further

and the emulsification found when determining solubilities at high salt concentrations was undoubtedly due to the low I.T.

I.T. measurements were also made at the 0.367M soap/"Nujol" interface, but due to wetting difficulties the usual procedure had to be modified, and the "Nujol" allowed to rise through the soap solution. The following values of the I.T. (dyn./cm.) were obtained:

	Soap Alone	C_6H_5Cl Present to give Max. η	Saturated with C_6H_5Cl
No salt	5.2	—	3.65
0.17M NaCl ..	4.0	3.45	2.4

indicating that the chlorobenzene molecules have an appreciable tendency to form a mixed film with the soap molecules (see also below).

From the viscosity and sedimentation velocity results, and the marked streaming birefringence of the very viscous solutions, the following would seem to be a reasonable hypothesis: progressive addition of chlorobenzene (or other non-polar organic molecule) to an aqueous soap/salt solution gradually changes the original approximately spherical micelles into highly asymmetric mixed aggregates which, when about half-saturated with chlorobenzene, begin to revert again to an approximately spherical shape. It is not yet possible to decide whether the asymmetric aggregates are rod-like or plate-like, but the former would seem to be the more likely.

If the aggregates are cylindrical rods having hemispherical ends, then the radius of the cylinder may be expected to approximate to the radius of the spheres (see above) from which it is formed. The surface area of a cylinder formed from n spheres is *less* than the total area of the original spheres, the relative decrease in area being equal to $(n-1)/3n$. If, therefore, the chlorobenzene is held mainly on the surface of the aggregate, as is indicated by the foregoing I.T. data, the molecular ratio of chlorobenzene to soap should increase as the maximum viscosity (that is, the axial ratio) decreases. The present results are in qualitative agreement with this picture, for example, 0.118M soap solutions (see inset, Fig. 3):

Max. Viscosity (cS.)	Molecular Ratio (Chlorobenzene/Soap) at Max. Viscosity
450	0.67
100	0.94
10	1.1

Some estimate of the axial ratio in the most viscous solutions may be obtained from the viscosity of concentrated solutions of high polymers in good solvents. Using the data of Ferry (1942), for example, this would indicate an axial ratio of several hundreds for the systems containing 1M NaCl.

(iv) *The Solubility of Chlorobenzene in C.P.Cl/NaCl Mixtures.*—Figure 4 shows the saturation solubility of chlorobenzene (expressed as g./l. of the original soap solution) in solutions of C.P.Cl containing various concentrations of salt. The form of the curve when there is no salt present is very similar to that for the system *trans*-azobenzene/C.P.Cl (see Fig. 1). In both instances the molecular

ratio begins to increase at a soap concentration of about $0.1M$, that is, when the separation of the centres of the micelles is about 90 \AA .

Low concentrations of salt enhance the solubility of chlorobenzene in C.P.Cl, but at higher salt concentrations the solubility decreases. This point is illustrated in Figure 5, only two soap concentrations being plotted for reasons of

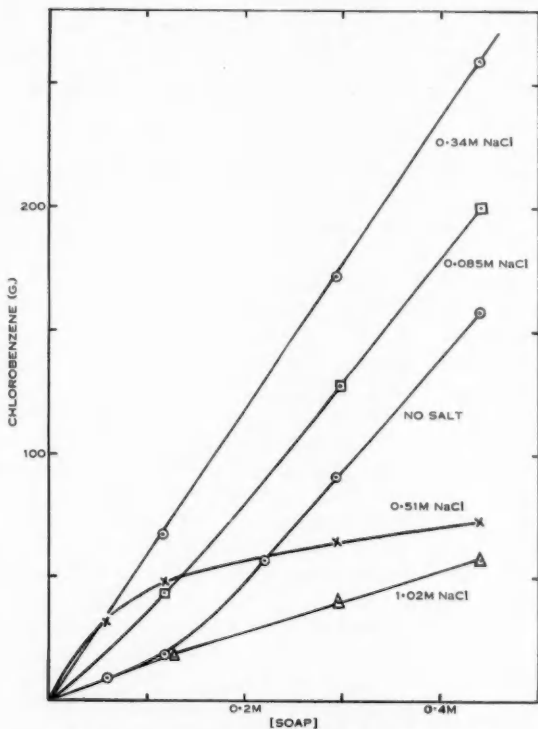


Fig. 4.—The saturation solubility (g./l. original soap solution) of chlorobenzene in cetyl pyridinium chloride solutions containing various concentrations of sodium chloride.

clarity. The maximum occurs at a salt concentration of *c.* $0.4M$. (A similar result has been found (McBain and Richards 1948) for the system benzene/C.P.Cl in the presence of various simple electrolytes.) Over the range 0.4 – $0.7M$ NaCl the solubility of chlorobenzene decreases, and salt concentrations above $0.7M$ NaCl have little further effect.

The sedimentation velocity measurements given above indicate that the aggregates in C.P.Cl/salt mixtures saturated with chlorobenzene are probably approximately spherical in shape, and it would thus seem unlikely that the striking changes in solubility arise from changes in *shape* of the aggregates.

Assuming approximately spherical particles, the observed changes in saturation solubility could arise from

- (1) changes in the radius of the micelle, without change in the number of soap molecules per micelle, or
- (2) changes in the concentration of micelles, due to changes in the number of soap molecules per micelle.

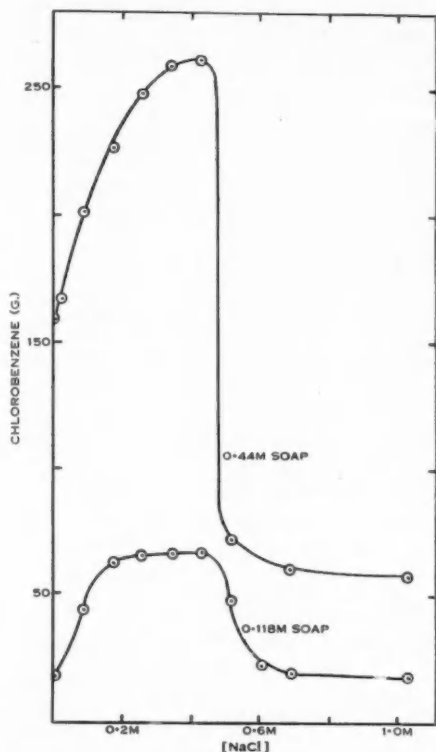


Fig. 5.—The effect of sodium chloride concentration upon the saturation solubility of chlorobenzene in cetyl pyridinium chloride solutions of strength 0.44 and 0.118M.

It is not possible, from the evidence at present available, to decide between these two alternatives.

V. ACKNOWLEDGMENTS

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THE RAMAN SPECTRA OF SOME AROMATIC SULPHONYL HALIDES

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Summary

The Raman spectra of benzene-, *p*-chlorobenzene-, *p*-bromobenzene-, *p*-methoxybenzene-, and *o*-, *m*-, and *p*-toluene sulphonyl chlorides and fluorides and methylbenzene sulphonate are recorded as well as the infra-red absorption bands of liquid benzene sulphonyl chloride and fluoride between 650 and 3100 cm^{-1} . A frequency *c.* 375 cm^{-1} is characteristic of the S-Cl bond in sulphonyl chlorides and a strong band at *c.* 1210 cm^{-1} is characteristic of the sulphonyl fluoride group. A Raman band at *c.* 1030 cm^{-1} in the chlorides and *c.* 1095 cm^{-1} in the fluorides appears to be associated with aromatic sulphonyl derivatives. There is such a band at 1094 cm^{-1} in the Raman spectrum of methylbenzene sulphonate.

I. INTRODUCTION

In an earlier paper (Ham and Hambly 1953) it was shown that a strong band at 377 cm^{-1} in the Raman spectrum of methane sulphonyl chloride was due to the S-Cl stretching frequency, while a strong band at 1210 cm^{-1} in both the infra-red and Raman spectra of methane sulphonyl fluoride was characteristic of the $-\text{SO}_2\text{F}$ group but was probably not a simple S-F stretching frequency. The Raman spectra of a series of aromatic sulphonyl chlorides and sulphonyl fluorides have now been studied to show that such bands are characteristic of the sulphonyl chloride and sulphonyl fluoride groups.

II. EXPERIMENTAL

The apparatus used was that previously described (Ham and Hambly 1953). Under the intense illumination from the mercury lamps, aromatic sulphonyl chlorides undergo slight photochemical decomposition and become turbid. This turbidity greatly increases the background intensity of the recorded Raman spectrum and obscures weak bands. It was found that this turbidity does not occur if approximately 10 per cent. of acetone is dissolved in the sulphonyl chloride. Compounds which are solid at room temperature were investigated as saturated solutions in acetone. Such solutions were filtered twice through a G4 sintered glass plate before irradiation.

Benzene-, *p*-chlorobenzene-, *p*-bromobenzene- and *p*-methoxybenzene-sulphonyl chlorides were prepared by adding the corresponding aromatic compound to chlorosulphonic acid with vigorous stirring and cooling. The products were purified by double distillation with rejection of first and last fractions or by repeated crystallization.

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m-Toluene sulphonyl chloride was prepared by the method described by Jenkins and Hambly (1953). The *o*- and *p*-toluene sulphonyl chlorides were commercial samples purified by distillation under reduced pressure and by recrystallization from light petroleum respectively.

Sulphonyl fluorides were prepared from the corresponding sulphonyl chlorides by the method of Davies and Dick (1931). They were purified by distillation and/or recrystallization.

Methyl benzene sulphonate was prepared by appropriate modification of the method for the preparation of methyl *p*-toluene sulphonate in *Organic Syntheses* (Gilman 1932).

Acetone was dried over potassium carbonate for several days and then fractionated. The middle fraction was redistilled twice.

III. RESULTS AND DISCUSSION

(a) Benzene Sulphonyl Chloride and Fluoride

The Raman spectra of benzene sulphonyl chloride and fluoride were obtained from the pure liquids and from the liquids mixed with 10 per cent. of acetone to reduce the continuous background. The Raman frequencies observed are recorded in Table 1, together with the bands of their infra-red spectra in the region covered by a sodium chloride prism. The Raman bands of the fluoride at 530 and 799 cm^{-1} were obtained with the pure liquid but were not clearly resolved from the 523 and 784 cm^{-1} bands of acetone when the latter was also present.

Nisi (1930) has reported the main bands in the Raman spectrum of benzene sulphonyl chloride while Schreiber (1949) has investigated its infra-red spectrum, in carbon tetrachloride solution, between 1000 and 1500 cm^{-1} . The present determinations are in substantial agreement with those of Nisi except that three additional bands of low frequency (105, 243, 318 cm^{-1}) are recorded. There are significant differences, however, between the infra-red bands found in a film of the pure liquid and those recorded by Schreiber for a dilute solution.

Kohlrausch and co-workers in a series of papers (for summary see Hibben 1939) showed that monosubstitution derivatives of benzene gave rise to six Raman bands characteristic of the aromatic structure. These lie at approximately 610, 1000, 1160, 1590, and 3045–3070 cm^{-1} . Such frequencies were found in the benzene sulphonyl halides examined. The infra-red band corresponding to the strong Raman band at c. 1590 cm^{-1} was extremely weak in the fluoride absorption spectrum and was not observed in that of the chloride. This symmetrical vibration (ν_{1g}) is inactive in the infra-red spectrum of benzene. On the other hand, no Raman band was observed in either substance corresponding to the strong infra-red band at 680 cm^{-1} which is due to a vibration (ν_4) which is inactive in the Raman spectrum of benzene.

The vibrations characteristic of the sulphonyl halide group are discussed below. In general, they are at somewhat higher frequencies than in the corresponding methane sulphonyl halides.

(b) *Methyl Benzene Sulphonate*

The Raman spectrum was obtained with the pure liquid and the frequencies are shown in Table 1. As expected, there are no bands in the neighbourhood

TABLE I
VIBRATION SPECTRA

$C_6H_5SO_2Cl$		$C_6H_5SO_2F$		$C_6H_5SO_2OCH_3$	Assignment
Infra-red (cm^{-1})	Raman (cm^{-1})	Infra-red (cm^{-1})	Raman (cm^{-1})	Raman (cm^{-1})	
	105 (s.) 243 (m.) 287 (m.)		134 (s.) 288 (m.) 321 (s.) 352 (w. diff.)	217 (w.) 316 (m.)	Aromatic S-Cl
	318 (m.) 373 (v.s.) 462 (m.) 575 (m. diff.) 608 (w.)		530 (v.w. diff.) 588 (m.) 610 (s.)	581 (m.) 609 (m.)	
680 (s.)		683 (v.s.)			SO ₂ deformation Aromatic (Raman inactive)
719 (s.)	716 (w.)	718 (v.s.)	716 (s.)	706 (s.)	C-S
757 (m.s.)		753 (v.s.) 786 (v.s.)	779 (w. diff.)	786 (m.)	
934 (v.w.)		934 (v.w.)			
998 (m.)	996 (v.s.)	1003 (w.)	1000 (v.s.)	999 (v.s.)	Aromatic
1022 (m.)	1024 (m.)	1026 (m.) 1074 (m.)	1023 (m.)	1024 (w.)	Aromatic
1082 (m.s.)	1079 (w.)	1100 (m.s.)	1097 (m.)	1094 (m.)	Aromatic sulphonyl
1178 (v.s.)	1167 (s.)	1169 (w.)	1162 (s.)	1174 (s.)	Aromatic
1190 (v.s.)	1184 (v.s.)	1180 (m.) 1205 (v.s.)	1179 (m.) 1212 (v.s.)	1185 (s.)	SO ₂ symmetric 'S-F'
1293 (w.)					
1380 (v.s.)	1375 (w.)	1420 (v.s.)	1409 (w. diff.)	1361 (w. diff.)	SO ₂ asymmetric
		1455 (v.s.)	1453 (v.w.)		
	1579 (s.)	1589 (v.v.w.)	1587 (s.)	1587 (s.)	Aromatic
				2963 (m.)	C-H (aliphatic)
3060 (w.)	3069 (s.)	3061 (w.)	3076 (v.s.)	3072 (s.)	C-H (aromatic)

of 375 or 1210 cm^{-1} . The usual aromatic frequencies are present as well as that of the C-H vibration in the methyl group at 2963 cm^{-1} . Table 1 is arranged to show the correlation of frequencies in this compound with those of the benzene sulphonyl halides.

(c) *Toluene Sulphonyl Halides*

The frequencies of the Raman bands for *o*-, *m*-, and *p*-toluene sulphonyl chlorides and fluorides are recorded in Table 2. *p*-Toluene sulphonyl chloride

TABLE 2
RAMAN SPECTRA OF TOLUENE SULPHONYL CHLORIDES AND FLUORIDES

<i>Ortho</i> -		<i>Meta</i> -		<i>Para</i> -	
Chloride	Fluoride	Chloride	Fluoride	Chloride	Fluoride
111 (s.)	126 (v.s.)		126 (s.)	85 (s.)	
268 (m.)	202 (m.)	224 (m. diff.)	217 (m.)	219 (w.)	213 (w. diff.)
			282 (s.)		
286 (m.)	297 (s.)	279 (m.)	296 (w.)	280 (s.)	291 (s.)
313 (m.)	319 (m.)	305 (m.)	326 (m.)		
352 (w.)			388 (w.)	350 (v.w.)	
373 (v.s.)		369 (v.s.)		373 (v.s.)	
438 (w. diff.)	413 (m.)		421 (v.w. diff.)		
495 (s.)	496 (m.)	496 (s.)	492 (m.)	480 (m.)	
532 (s.)	544 (s.)	514 (w.)	524 (s.)	526 (m.)	
567 (s.)			556 (w. diff.)		
584 (s.)	596 (m.)	587 (s.)	591 (m.)	573 (s.)	
633 (w. diff.)	631 (w.)			627 (m.)	629 (m.)
				650 (w.)	659 (m.)
687 (s.)	691 (v.s.)	691 (m.)	696 (v.s.)		700 (m. diff.)
	762 (m. diff.)				766 (s.)
806 (s.)	813 (s.)	791 (w.)		805 (v.w.)	813 (m.)
		852 (w.)	872 (s.)		
		994 (v.s.)	1001 (s.)		
1043 (v.s.)	1050 (v.s.)	1026 (v.w.)			
		1082 (m.)			
1078 (w.)	1099 (m.)	1108 (m.)	1095 (s.)	1081 (s.)	1097 (s.)
1171 (v.s.)	1148 (w.)		1143 (m.)	1153 (v.s.)	
1183 (v.s.)	1178 (s.)	1169 (v.s.)	1169 (s.)	1172 (v.s.)	1184 (v.s.)
1204 (w.)	1209 (v.v.s.)	1221 (m.)	1203 (s.)	1212 (w.)	1205 (v.v.s.)
1368 (m. diff.)	1391 (m.)		1387 (m.)	1338 (w.)	1380 (w. diff.)
1382 (m. diff.)	1402 (m. diff.)	1384 (w.)	1405 (m.)	1379 (w.)	1412 (w. diff.)
			1425 (m.)	1439 (w.)	
1574 (s.)	1580 (s.)	1578 (s.)	1583 (v.s.)		
1599 (v.s.)	1600 (v.s.)	1592 (w. diff.)	1603 (s.)	1595 (v.s.)	1596 (s.)
2931 (s.)	2948 (m.)	2925 (w.)	2928 (s.)	?	?
3074 (s.)	3077 (s.)	3073 (w.)	3072 (s.)	3075 (m.)	3069 (s.)

and *p*-toluene sulphonyl fluoride which are solids at room temperature were irradiated in acetone solutions of concentration 60 and 80 per cent. (w/v) respectively. As a result the C-H frequency of the methyl group was not resolved from the corresponding strong acetone band at 2922 cm.⁻¹. The

aromatic band at $c. 1580$ is, as usual, split into two components in the *o*- and *m*-derivatives, but not in the *p*-toluene sulphonyl chloride and fluoride which can have a plane of symmetry at right angles to the plane of the aromatic ring. The weak bands in the region just beyond 1200 cm^{-1} in the toluene sulphonyl chlorides are not found in the other aromatic sulphonyl chlorides examined and are not likely to cause any confusion with the very strong band in this region which is associated with the sulphonyl fluoride group.

(d) *Miscellaneous Sulphonyl Chlorides and Fluorides*

p-Chloro- and *p*-bromobenzene sulphonyl chlorides were studied as 60 per cent. (w/v) solutions in acetone and the corresponding fluorides as 50 per cent.

TABLE 3
RAMAN SPECTRA OF MISCELLANEOUS SULPHONYL HALIDES

$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{Cl}$	$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{F}$	$p\text{-BrC}_6\text{H}_4\text{SO}_2\text{Cl}$	$p\text{-BrC}_6\text{H}_4\text{SO}_2\text{F}$	$p\text{-CH}_3\text{O.C}_6\text{H}_4\text{SO}_2\text{F}$
220 (m.) 254 (m.) 351 (m.) 374 (v.v.s.) 467 (m.) 487 (w.) 527 (w.) 565 (m.) 600 (s.) 617 (m.) 753 (m.) 1083 (v.s.) 1094 (v.s.) 1158 (m.) 1172 (v.s.) 1183 (v.s.) 1404 (w. diff.) 1581 (v.s.) 3081 (w.)	159 (m.) 341 (m.) 626 (w.) 748 (m.) 1093 (s.) 1160 (s.) 1197 (m.) 1212 (s.) 1591 (s.) 3090 (m.)	211 (m.) 373 (v.s.) 417 (w.) 480 (m.) 585 (s.) 614 (w.) 735 (w.) 1068 (v.s.) 1078 (s.) 1157 (v.s.) 1174 (s.) 1183 (s.) 1570 (v.s.) 3074 (w.)	184 (m.) 213 (s.) 529 (m.) 618 (s.) 734 (s.) 1069 (s.) 1095 (s.) 1158 (s.) 1181 (m.) 1213 (s.) 1579 (v.s.) 3070 (m.)	505 (m.) 539 (w.) 557 (m.) 623 (w.) 662 (w.) 707 (w.) 761 (m.) 803 (m.) 1006 (v.v.) 1030 (w. diff.) 1090 (s.) 1101 (s.) 1167 (v.s.) 1212 (m.) 1270 (w.) 1319 (w. diff.) 1582 (s.) 1596 (v.s.) 3085 (w.)

(w/v) solutions in the same solvent. *p*-Methoxybenzene sulphonyl fluoride was irradiated without addition of acetone. All these compounds gave a fairly strong continuous background in the spectrum and we believe that some weak



bands have not been recorded in Table 3. *p*-Nitrobenzene sulphonyl fluoride, which is much less soluble in acetone than the other sulphonyl fluorides which we have studied, yields a pale yellow solution (22 per cent. w/v) which gives a strong absorption of the incident radiation, 4358 Å. Only four bands due to the solute were recorded with sufficient intensity for measurement, but these included the sulphonyl fluoride band at 1217 cm^{-1} and the 1352 cm^{-1} band characteristic of the nitro-group. The other frequencies observed were 1099 and 1590 cm^{-1} .

(e) *Characteristic Frequencies of Sulphonyl Derivatives*

(i) *SO₂ Deformation Band*.—This vibration gives rise to bands at 531 and 538 cm^{-1} in methane sulphonyl chloride and fluoride respectively. In the corresponding benzene derivatives the deformation vibration is displaced to higher frequencies 575, 588 cm^{-1} probably due to the enhanced polarization of the S-O bonds increasing the electrostatic repulsion between the oxygen atoms.

TABLE 4
RAMAN FREQUENCIES CHARACTERISTIC OF SULPHONYL DERIVATIVES

Compound	SO ₂ Deforma- tion	SO ₂ Sym. Stretch	SO ₂ Asym. Stretch	S-X	C-S	Aromatic Sulphonyl
CH ₃ SO ₂ Cl ..	531	1168	1361	377	748	—
C ₆ H ₅ SO ₂ Cl ..	575	1184	1375	373	716	1079
<i>o</i> -CH ₃ C ₆ H ₄ SO ₂ Cl ..	584	1183	1368	373	687	1078
<i>m</i> -CH ₃ C ₆ H ₄ SO ₂ Cl ..	587	1169	1384	369	691	1082
<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ Cl ..	573	1172	1379	373	650 ?	1081
<i>p</i> -ClC ₆ H ₄ SO ₂ Cl ..	565 ?	1183 (1172)		374	753	1094 (1083)
<i>p</i> -BrC ₆ H ₄ SO ₂ Cl ..	585	1183 (1174)		373	735	1078 (1068)
CH ₃ SO ₂ F ..	538	1186	1401	1210	738	—
C ₆ H ₅ SO ₂ F ..	588	1179	1409	1212	716	1097
<i>o</i> -CH ₃ C ₆ H ₄ SO ₂ F ..	596	1178	1402	1209	691	1099
<i>m</i> -CH ₃ C ₆ H ₄ SO ₂ F ..	591	1169	1405	1203	696	1095
<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ F ..		1184	1412	1205	700 (659)	1097
<i>p</i> -ClC ₆ H ₄ SO ₂ F ..		1197		1212	748	1093
<i>p</i> -BrC ₆ H ₄ SO ₂ F ..		1181		1213	734	1095 (1065)
<i>p</i> -CH ₃ OC ₆ H ₄ SO ₂ F ..	557 ?	1167		1212	707	1090
C ₆ H ₅ .SO ₂ .OCH ₃ ..	581	1185	1361		706	1094

The identification of the corresponding frequency in the substituted aromatic sulphonyl halides is not free of ambiguity since there is often more than one frequency in this region, but the tentative assignments made in Table 4 (column 1) appear to be highly probable.

(ii) *SO₂ Symmetrical Stretch*.—This vibration in both the aromatic sulphonyl chlorides and fluorides lies in the region *c.* 1180 cm^{-1} whereas in the methane derivatives it lies at 1168 cm^{-1} for the chloride and 1186 cm^{-1} for the fluoride.

It is usually well resolved from the aromatic band at $c. 1160 \text{ cm}^{-1}$ but two frequencies in this region were not observed with *m*-toluene sulphonyl chloride or *p*-methoxybenzene sulphonyl fluoride. In *p*-chloro- and *p*-bromobenzene sulphonyl chloride where the parent compounds have two frequencies (chlorobenzene $1157, 1174 \text{ cm}^{-1}$; bromobenzene $1163, 1177 \text{ cm}^{-1}$) in this region the S-O vibration is still resolved as a third band (1183 cm^{-1}). The general increase in this frequency in the aromatic sulphonyl chlorides agrees with the increase in the corresponding deformation frequency but the sulphonyl fluorides show practically the same value as in the aliphatic compounds and no increase over the value in the sulphonyl chlorides. The infra-red spectra are compared in Figure 1.

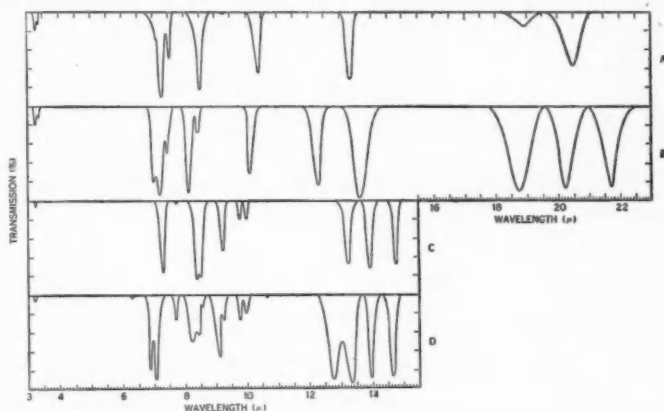


Fig. 1.—Infra-red spectra of methane sulphonyl chloride (A); methane sulphonyl fluoride (B); benzene sulphonyl chloride (C); and benzene sulphonyl fluoride (D).

(iii) *SO₂ Asymmetrical Stretch*.—This band is, as expected, weak in the Raman spectrum but strong in the infra-red spectrum of the benzene derivatives. It was not observed in a number of compounds which give a fairly strong continuous spectrum, nor could it be assigned unambiguously in the toluene derivatives since the symmetrical deformation of the methyl group gives a band with about the same frequency.

(iv) *Sulphur-Halogen Vibration Frequencies*.—All the sulphonyl chlorides showed the S-Cl stretching vibration as a band of high intensity which only varied between 369 and 377 cm^{-1} in the seven chlorides listed in Table 4. The characteristic strong S-F band varied from 1203 to 1213 cm^{-1} in the eight sulphonyl fluorides. As previously stated (Ham and Hambly 1953), this frequency is almost certainly not due to a simple S-F stretching vibration but is characteristic of a motion in which both oxygen and fluorine atoms are involved.

(v) *Carbon-Sulphur Vibration Frequencies*.—Trotter and Thompson (1946) and Sheppard (1950), from a study of the infra-red spectra of a series of aliphatic sulphides, disulphides, and thiols, concluded that the C-S stretching frequency

was very variable but lay between 600 and 700 cm^{-1} . Cymerman and Willis (1951) attribute a frequency of 670–700 cm^{-1} to this vibration in the infra-red spectra of a series of aromatic disulphides, sulphones, and thiosulphonates. On the other hand, Houlton and Tartar (1938) assign a frequency 760–890 cm^{-1} to this linkage in the Raman spectra of sodium alkyl sulphonates. In benzene sulphonyl chloride and fluoride we do not experience the ambiguity found by Cymerman and Willis (1951) in their infra-red spectra, in that the ν_4 vibration of the aromatic nucleus is not recorded in the Raman spectrum so that there is little doubt that the 716 cm^{-1} vibration is that of the C–S linkage. In the substituted sulphonyl halides the value of the frequency seems to increase with increased electron attraction by the second substituent. The value of 650 cm^{-1} for *p*-toluene sulphonyl chloride, however, seems anomalous.

(vi) *The 1080–1095 cm^{-1} Bands.*—All the aromatic sulphonyl halides examined show a band at *c.* 1080 cm^{-1} in the chlorides and *c.* 1095 cm^{-1} in the fluorides. There is a similar band at 1094 cm^{-1} in the Raman spectrum of methyl benzene sulphonate. Monosubstituted aromatic molecules do not usually produce a band in this region though in the case of chlorobenzene and bromobenzene bands are found at 1083 and 1073 cm^{-1} respectively. However, with *p*-chlorobenzene sulphonyl chloride and *p*-bromobenzene sulphonyl chloride and fluoride two frequencies are present in this portion of the spectrum, one of which can be associated with the presence of the sulphonyl group. We tentatively suggest that this band, which is not found with the methane sulphonyl halides previously examined, is characteristic of aromatic sulphonyl derivatives and propose to examine the Raman spectra of a number of aromatic and aliphatic sulphonic esters to test this hypothesis.

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THE REACTION BETWEEN ACETONE AND AMMONIA

III. REDUCED PYRIDINE DERIVATIVES

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Summary

The preparation of 2,2,4,6-tetramethyldihydropyridine by the reaction of acetone and ammonia at temperatures of 100–180 °C. has been studied; using an alkaline catalyst at 120 °C. for 3 hr. a yield of over 60 per cent. can be obtained. This dihydropyridine is identical with the product obtained by Matter (1948) in the pyrolysis of 2,2,4,4,6-pentamethyltetrahydropyrimidine. Possible mechanisms for its formation are discussed. Catalytic hydrogenation over Raney nickel leads to tetramethylpiperidine, while with palladium a partial reduction product, formulated as 2,2,4,6-tetramethyl-2,3,4,5-tetrahydropyridine is obtained; the chemistry of these reduction products has been examined.

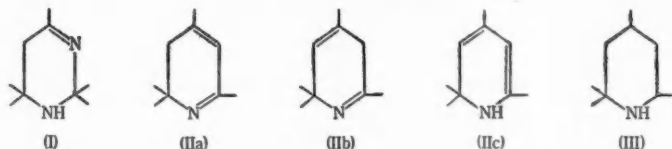
I. INTRODUCTION

The reaction between acetone and ammonia at room temperature in the presence of an acid catalyst has been shown (Bradbury, Hancox, and Hatt 1947) to yield 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine (I) in high yield. Matter (1948) investigating the reaction concurrently, has shown that pyrolysis of this pyrimidine in the presence of acidic substances (ammonium chloride, silica gel) gives a tetramethyldihydropyridine which he formulates as IIa, b, or c. It has now been shown that this same dihydropyridine is produced directly from acetone by heating with excess of liquid ammonia in the presence of a strong alkali, the yield, with the best conditions, exceeding 60 per cent. It can also be prepared using an acid catalyst, but the yield is diminished by the simultaneous formation of I; under alkaline conditions this is entirely suppressed. In either method, II is accompanied by varying quantities of high-boiling material, presumably polymers. With the alkaline catalyst 3 hr. heating at 120 °C. was found to give the best results, with a 63 per cent. yield of II and about 30 per cent. of high-boiling material. The base II is a pale yellow liquid of b.p. 51–52 °C. at 12 mm. which rapidly darkens and resinifies on exposure to air, but is stable in an inert atmosphere. Matter reports a platinichloride as the only stable salt, but in the present work, although no hydrochloride could be obtained, a stable orange-yellow picrate was readily prepared. Attempts to obtain other derivatives, for example, by diene reaction, were unsuccessful.

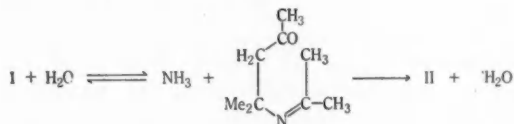
Matter suggests a mechanism for the pyrolysis of I through an open-chain intermediate of rather unlikely allene structure. It might be postulated that the formation of II in the high-temperature acid-catalysed synthesis depends

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on the prior formation of I and its gradual pyrolysis under the acidic conditions (acetone + ammonia \rightarrow I \rightarrow II), but it is difficult to sustain such an explanation for the alkali-catalysed reaction; both the known stability of I to heat in the presence of alkalis, and the absence of I in the product are against such a scheme.



It seems more probable that the acid-catalysed synthesis consists in the production of I and II by parallel reactions involving a common intermediate, such as diacetonamine, with higher temperatures favouring the reaction leading to II (see Table 1). In the alkali-catalysed synthesis, there is no competing reaction leading to I, and a rather lower temperature gives best results, causing less destruction of II by heat while still allowing its formation to proceed at a reasonable rate. To explain the formation of II from I by pyrolysis under mildly acid conditions, as in Matter's experiments, it is only necessary to assume hydrolysis by a little water to cause ring opening and loss of one molecule of ammonia, followed by a new, aldol-type ring closure:



The direct synthesis of II may be considered as a simple variant of the Chichibabin pyridine synthesis. As normally applied to aldehydes, the final step of this synthesis is regarded as a dehydrogenation of a dihydropyridine intermediate, some of the aldehyde acting as a hydrogen acceptor. When, however, a ketone reacts, the presence of a quaternary carbon atom precludes such a dehydrogenation, and in the present reaction with acetone the dihydropyridine is, in fact, isolated. Aromatization of II could proceed only by elimination of methane; Riehm's (1887) synthesis of 2,4,6-collidine from acetone and ammonium chloride at 265 °C. undoubtedly supplies this further step.

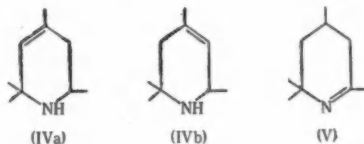
Matter's proof of the carbon skeleton of II rests on the synthesis of its partial reduction product from 2,2,6-trimethyl-4-piperidone* and methyl magnesium iodide; the present work confirms its correctness. The position of the double bonds however, is uncertain, for the product of the Grignard synthesis need not have the double bond in the position shown in IVa.

Matter prepared from II by reduction with sodium and alcohol a mixture of 2,2,4,6-tetramethylpiperidine (III) and a tetrahydropyridine which he regards

* Vinyldiacetonamine. The old trivial names in this series, antedating systematic nomenclature, are misleading, and particularly so in this instance. It would be well to abandon them.

as IVa, separation of which required fractionation of the mixed hydrochlorides. It has been found that catalytic hydrogenation of II can be performed so that, under the appropriate conditions, either the completely reduced piperidine (III) or a new tetrahydropyridine (V) is the sole product.

Hydrogenation of II using Raney nickel under mild conditions gave only a mixture of III and V, which could be separated by making use of the different solubilities of their picrates in ethanol; with this catalyst it was impossible to interrupt the reaction at a stage where V alone was produced. At 120 °C. and 100 atm. complete hydrogenation to III occurred. The partial hydrogenation to pure V was readily effected with a palladium-on-carbon catalyst at 50–60 °C.; absorption of 1 mol. of hydrogen proceeded very rapidly and the reaction then stopped.

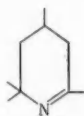


The base III obtained as described above appears identical with the saturated product from the sodium reduction; the melting points of the picrate and hydrochloride were found notably higher than recorded by Matter, but this is explicable in view of the difficulty of obtaining a pure product by fractional crystallization. Steric inhomogeneity is possible in the product obtained by either process, but no separation of isomers could be achieved.

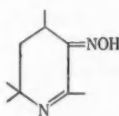
The base III behaves as a secondary amine, having its reactivity depressed by the steric hindrance of the flanking methyl groups. It forms liquid *N*-nitroso- and *N*-acetyl derivatives without difficulty, but is completely resistant to aroylation by the Schotten-Baumann procedure. A *p*-nitrobenzoyl derivative can be formed by reaction with *p*-nitrobenzoyl chloride in dry benzene at 120 °C. Methyl magnesium iodide evolves no methane in a Zerevitinov estimation. Somewhat surprisingly, however, phenyl isocyanate reacts readily to give an *N*-phenylurea and this is the most suitable derivative for characterization. High steric hindrance has been reported several times in related compounds: thus Leonard and Nommensen (1949) found that benzoylation of 2,2,6,6-tetramethylpiperidine needed 72 hr. refluxing with benzoyl chloride in benzene; Singer and McElvain (1935) found that 2,6-dimethylpiperidine reacted with *n*-butyl bromide in light petroleum at 90 °C. to the extent of only 5 per cent. in 48 hr., and Bell, Strickland, and Wright (1951) describe the extreme hindrance of the carbonyl group in 2,2,6-trimethylcyclohexanone.

The unsaturated base V is a colourless mobile liquid boiling at 155–156 °C. It becomes yellow and slowly resinifies on exposure to air, but keeps well in stoppered vessels. Its characteristic picrate, in contrast to the orange picrates of III and IV, is lemon-yellow and markedly less soluble in alcohol, thus resembling the picrate of II.

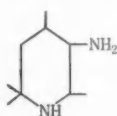
The Δ^1 -piperidein structure assigned to V appears the most satisfactory in the light of the evidence adduced below. First, the mode of formation is significant—palladium catalysts are known to be relatively inactive towards carbon-nitrogen multiple bonds (compare their use in the hydrogenation of unsaturated to saturated nitriles)—(Allen and Drewitt 1950). Secondly, the observed molecular refraction (44.23) favours this structure (44.24) rather than that of an isomer with a carbon-carbon double bond (44.70). Further no derivatives of a secondary amine could be obtained. Nitrous acid does indeed give a crystalline derivative, m.p. 171 °C., of formula $C_6H_{10}N_2O$, but it is clearly not a nitrosamine for it is amphoteric, forming crystalline salts with acids, and giving a solution with alkalis from which it can be regenerated with carbon dioxide; and it readily gives an unstable benzoyl derivative. Thus it is closely analogous to the compound obtained from the reaction of nitrous acid with I (Hancox 1950). The oximino-structure VI is further confirmed by its reduction with Raney nickel and hydrogen to a diamine VII. Finally, V can be synthesized from III by dehydrochlorination of the *N*-chlorimine of III.



(V)



(VI)



(VII)

Until the recent work of Schöpf *et al.* (1948) and Schöpf, Arm, and Krumm (1951) there has been little reliable information about Δ^1 -piperideins. Usually it has been assumed that they will be indistinguishable by reason of tautomerism from the Δ^2 -piperideins, of which a number has been reported by early workers. But the position of the double bond in these reported Δ^2 -piperideins does not rest on any very conclusive evidence; mostly this is evidence from their formation by ring-closure synthesis, where the double bond might just as rationally be assigned to the Δ^1 - as the Δ^2 -position. Among recent workers on the related pyrrolines, there is a growing conviction that the majority of compounds previously formulated with the Δ^2 -structure are in reality Δ^1 -pyrrolines (cf. Prelog *et al.* 1951); chemical and physical evidence has recently been obtained for this view (Evans 1951; McGinnity and Cloke 1951). The last-named authors show by Zerevitinov analysis that pyrrolines prepared by ring-closure synthesis from δ -chlorovaleronitriles have no "active-hydrogen" atom. This method, unfortunately, yields no information about the structure of V, since neither it nor the fully saturated piperidine III reacts with methyl magnesium iodide; steric hindrance is presumably responsible for the inertness of the hydrogen in III.

Schöpf's recent work on the unsubstituted bases Δ^1 -piperidein and Δ^1 -pyrroline shows that these compounds are completely stable at room temperature at pH values below 2 and above 12, but in the intermediate region undergo spontaneous polymerization to a variety of trimers. No such ready polymerization was noted with V; here also, one would expect that the methyl

substituents would profoundly hinder the formation of such tetracyclic polymers as are described by Schöpf.

No tendency for V to react in an open-chain aminoketone form was observed. Reaction in the aminoketone form in the presence of water is the most characteristic behaviour of the tetrahydropyridines described in the literature as Δ^2 -piperideins; for example, nitrous acid, benzoyl chloride, and hydroxylamine give open-chain derivatives. Evans (1951) has also observed the formation of an open-chain benzoyl derivative from the 2-methylpyrroline which he regards as existing entirely in the Δ^1 -structure. However, repeated attempts to prepare open-chain derivatives of V have been fruitless.

II. EXPERIMENTAL

Melting points are corrected. The microanalyses were carried out in the Microanalytical Laboratory, Division of Industrial Chemistry, under the direction of Dr. W. Zimmermann.

(a) *2,2,4,6-Tetramethyldihydropyridine (II).*—(i) *Acid-catalysed Reaction.* Acetone (290 g.; 5 mol.), ammonia (102 g.; 6 mol.), calcium chloride (10 g.), and ammonium chloride (10 g.) were charged into a rotating autoclave fitted with stainless steel rods for stirring, and heated to temperatures and for periods indicated in Table 1. After quenching and cooling to room temperature, the upper organic layer was withdrawn and taken up in 300 ml. of light petroleum (b.p. 40–60 °C.). The petroleum solution was then cooled to 0 °C. and extracted with ice-cold water (150 ml. + 4 portions of 40 ml.) to remove excess ammonia and the pentamethyltetrahydropyrimidine formed as a by-product. After drying (Na_2SO_4), and removal of the solvent through a short column the residue was fractionated at 12 mm. pressure. The tetrahydropyridine was obtained as the first fraction (b.p. 50–51 °C./12 mm.); the residue boiled over a wide range from about 90 °C., without separation into sharp fractions—the mixture of products is thus similar to that obtained by Matter in the pyrolysis of 2,2,4,4,6-pentamethyltetrahydropyrimidine. Yields are shown in Table 1.

TABLE I

Temperature (°C.)	Time (hr.)	Yield of Dihydropyridine (%)	Yield of Higher Fractions (%)
120	5	9	24
120	10	12	46
150	5	20	32
150	10	22	53
190	1	16	17
190	2	20	28
190	3	22	56

(ii) *Alkali-catalysed Reaction.*—The quantities of acetone and ammonia were the same as in (i). In place of the calcium chloride and ammonium chloride the catalyst used was either soda-lime, or better, a 40 per cent. aqueous solution of sodium hydroxide. After the experiments the reaction mixture was worked up as before. No pentamethyltetrahydropyrimidine was found in the water washings. Yields are shown in Table 2.

2,2,4,6-Tetramethyldihydropyridine formed a pale yellow, mobile liquid, immiscible with water, which rapidly darkened on exposure to air, and after a few hours became a dark, sticky

mass. If sealed at once into ampoules it may be kept indefinitely (Found: n_D^{25} 1.471; d_4^{25} 0.866; MR_D 44.2. Calc. for structure II, 43.8; neut. equiv., 138 (calc. for $C_8H_{16}N$, 137)).

The *picrate* was prepared by dropwise addition of the base to a slight excess of a saturated alcoholic solution of picric acid. Yellow, friable prisms from ethanol, m.p. 154°C. (decomp.) (Found: C, 49.1; H, 4.9; N, 15.3%. Calc. for $C_{15}H_{18}N_4O_7$: C, 49.2; H, 4.9; N, 15.3%).

Attempts to prepare a crystalline hydrochloride or hydrobromide were unsuccessful.

TABLE 2

Catalyst	Temperature (°C.)	Time (hr.)	Yield of Dihydropyridine (%)	Yield of Higher Fractions (%)
Soda-lime	180	3	39.3	41
" " "	180	2	38.8	39
" " "	150	3	45.4	34
" " "	120	3	56.7	19
" " "	120	2	54.6	17
Sodium hydroxide	120	3	62.7	17
" "	120	4	63.1	20
" "	Room	12	4.4	6

(b) 2,2,4,6-Tetramethylpiperidine (III).—2,2,4,6-Tetramethyldihydropyridine (50 g.) was hydrogenated in 50 ml. ethanol in the presence of Raney nickel at 110°C. at an initial hydrogen pressure of 1500 lb. After 2 hr., absorption of hydrogen was complete (2 mol.). The product (46 g.) was a colourless liquid with a nauseous odour, b.p. 155–157°C./770 mm., n_D^{25} 1.4374; d_4^{25} 0.816; MR_D (obs.) 45.34, (calc.) 45.16; neut. equiv., 142 (calc. for $C_8H_{18}N$, 141).

The *hydrochloride* was prepared by neutralization with conc. hydrochloric acid, followed by dehydration by refluxing with benzene in a Soxhlet apparatus holding a thimble of anhydrous magnesium sulphate. From ethanol it formed colourless needles, m.p. 215–216°C., very soluble in water, and sparingly soluble in acetone (Found: C, 60.9; H, 11.0; Cl, 20.1%. Calc. for $C_8H_{18}NCl$: C, 60.9; H, 11.3; Cl, 20.0%).

The *hydrobromide*, crystallized from ethanol, had m.p. 246–247°C. (Found: N, 6.3; Br, 35.9%. Calc. for $C_8H_{18}NBr$: N, 6.3; Br, 36.0%).

The *picrate*, prepared in benzene solution and recrystallized from benzene, formed orange rhombs, m.p. 188–189°C. (Found: C, 48.8; H, 5.8%. Calc. for $C_{18}H_{22}N_4O_7$: C, 48.6; H, 6.0%).

The *phenylurea*, prepared by reaction of the base with phenyl isocyanate in light petroleum, precipitated immediately as colourless needles; recrystallized from benzene-light petroleum it had m.p. 123°C. (Found: C, 74.1; H, 9.0; N, 11.0%. Calc. for $C_{16}H_{24}N_2O$: C, 73.8; H, 9.2; N, 10.8%). No derivatives could be prepared from the base III by the Schotten-Baumann method.

A *p*-nitrobenzoyl derivative was obtained in the following way: The base III (2.8 g.), and freshly prepared *p*-nitrobenzoyl chloride (1.85 g.) were dissolved in dry benzene (50 ml.) and the mixture heated in a pressure vessel at 120°C. for 4 hr. From the reaction mixture, 1.2 g. of base hydrochloride separated, and, after concentration of the filtrate followed by recrystallization of the product from acetone, 1.0 g. (35%) of *p*-nitrobenzoyl derivative was obtained. It formed thick prisms, m.p. 121°C. (Found: C, 66.6; H, 7.6; N, 10.0%. Calc. for $C_{16}H_{22}N_2O_4$: C, 66.2; H, 7.6; N, 9.7%). A very small yield of the same product was obtained from III and *p*-nitrobenzoyl chloride in pyridine.

The *acetyl derivative*, prepared by refluxing III with excess of acetic anhydride for $\frac{1}{2}$ hr., was a colourless liquid of somewhat camphraceous odour, b.p. 100–101 °C./5 mm. (Found: N, 7.8%. Calc. for $C_{11}H_{21}NO$: N, 7.7%).

(c) *2,2,4,6-Tetramethyltetrahydropyridine (V)*.—The base II (48 g.) in alcohol (50 ml.) was hydrogenated in the presence of 1 g. of 5% palladium on carbon catalyst reduced separately immediately before use. Hydrogenation occurred rapidly at 50–60 °C. and 1600 lb. pressure; after 10 min., 1 mol. of hydrogen was absorbed and no further reaction could be detected. The product (44 g.) was an almost colourless liquid of b.p. 155–156 °C./755 mm.; n_D^{25} 1.4460; d_4^{25} 0.838; MR_D 44.23 (calc. for structure V, 44.24; for alternative structure Va, 44.70); neut. equiv., 139 (calc. for $C_8H_{17}N$, 139). It slowly developed a reddish yellow colour in air, but in stoppered vessels underwent little alteration.

The *hydrochloride of V* was formed as colourless prisms from ethanol, m.p. 196 °C. (Found: C, 61.8; H, 10.3; Cl, 20.2%. Calc. for $C_8H_{16}NCl$: C, 61.5; H, 10.3; Cl, 20.2%).

The *hydrobromide of V* formed colourless prisms from ethanol, m.p. 216–217 °C.

The *picrate of V* formed lemon-yellow plates from ethanol, m.p. 151 °C. It is much less soluble in ethanol than the picrate of III (Found: C, 49.1; H, 5.7%. Calc. for $C_{18}H_{20}N_4O_7$: C, 48.9; H, 5.4%).

(d) *5-Oximino-2,2,4,6-tetramethyltetrahydropyridine (VI)*.—To the base V (14 g.) dissolved in 1:1 hydrochloric acid (25 ml.) was added a saturated aqueous solution of sodium nitrite (12 g.), and the mixture cautiously heated until reaction set in, and a brownish crystalline solid began to separate. After the spontaneous reaction had subsided, the mixture was boiled for 5 min. more, cooled, the product collected, and washed with water. If the initial reaction is allowed to become too vigorous, the product is contaminated with tarry material which is difficult to remove. After recrystallization from methanol (charcoal) it was obtained as colourless rhombs of m.p. 170.5–171 °C. Yield 11 g., 60%. It is readily soluble in aqueous alkali, from which it can be recovered unchanged on saturation with carbon dioxide (Found: C, 64.3; H, 9.6; N, 16.7%. Calc. for $C_8H_{16}H_2O$: C, 64.3; H, 9.5; N, 16.7%).

The *hydrochloride of VI* formed colourless needles from ethanol/ether, m.p. 235 °C. (decomp. after gradual darkening) (Found: Cl, 17.4%. Calc. for $C_8H_{17}N_2OCl$: Cl, 17.3%).

Benzoyl derivative of VI. This was prepared by the Schotten-Baumann method. After thorough washing, the crude product was recrystallized at once from acetone and then from ether. It was obtained as faintly greenish plates, m.p. 78–79 °C. The compound gradually darkened and decomposed in the course of about a week (Found: C, 70.5; H, 7.5; N, 9.9%. Calc. for $C_{14}H_{20}N_2O_2$: C, 70.6; H, 7.4; N, 10.3%).

(e) *5-Amino-2,2,4,6-tetramethylpiperidine (VII)*.—The oxime-base VI (22 g.) in 100 ml. of ethanol was hydrogenated in the presence of Raney nickel (W.7) at an initial pressure of 1400 lb. Absorption of hydrogen was rapid at 110–120 °C., and was complete in 15 min. with the consumption of 3 mol. After removal of solvent, the bulk of the product distilled at 81–82 °C./12 mm., with a small high-boiling residue. Yield 17 g., 85%; n_D^{25} 1.4670. It is a colourless, rather viscous liquid of nauseous odour. It is hygroscopic, and reacts avidly with atmospheric carbon dioxide (Found: neut. equiv., 80.0. Calc. for $C_8H_{20}N_2$ (diacid), 78.0).

The *dihydrochloride of VII* was obtained as a colourless microcrystalline powder from ethanol/ether, m.p. 300 °C. (Found: Cl, 31.2%. Calc. for $C_8H_{22}N_2Cl_2$: Cl, 31.0%).

The *dipicrate of VII* formed orange crystals from ethanol, decomp. c. 240 °C. (Found: C, 41.2; H, 4.2%. Calc. for $C_{21}H_{26}N_8O_{14}$: C, 41.0; H, 4.2%).

The *monobenzoyl derivative of VII*, obtained by the Schotten-Baumann method, formed colourless needles from acetone, m.p. 171 °C. (Found: C, 73.4; H, 9.2; N, 10.8%; neut. equiv. (titration in aqueous alcohol), 263. Calc. for $C_{14}H_{20}ON_2$: C, 73.8; H, 9.2; N, 10.8; neut. equiv., 260). The second amino-nitrogen could not be benzoylated; however, as was observed with III, it could be made to react with phenyl isocyanate.

Biphenylurea of VII, prepared in light petroleum, and recrystallized from benzene, m.p. 194 °C. (Found: C, 70.1; H, 7.6; N, 14.5%. Calc. for $C_{23}H_{26}N_4O_2$: C, 70.0; H, 7.6; N, 14.2%).

(f) *Conversion of III to V.*—III (14 g.) was converted to the acetate with glacial acetic acid, and sufficient water added to make a saturated solution. This was added over a period of 1 hr. to a solution of calcium hypochlorite (220 ml. of 0.88N) at 0–5 °C. with continuous stirring. The mixture was then extracted as rapidly as possible with four portions, each 200 ml., of ice-cold, peroxide-free ether. After drying (Na_2SO_4), the ether was distilled off from a water-bath maintained at 50 °C., the last traces being removed in a stream of nitrogen. The crude product weighed 15 g., and assayed 92% of chlorimine by iodometric titration.

The crude chlorimine was added during 5 min. to a boiling 10% solution of alcoholic potassium hydroxide (70 ml.). After the heat of reaction had subsided, the mixture was boiled a further 10 min. and then steam-distilled. The distillate was neutralized, concentrated to remove ethanol, and the product isolated by making alkaline and extracting with ether. Fractional crystallization of the picrate from alcohol removed unchanged III, and gave a picrate of m.p. 150–151 °C. undepressed by admixture with the picrate of V. From this, 5 g. of base, b.p. 155–156 °C., n_D^{25} 1.4454 was obtained.

(g) *Sodium Reduction.*—The unsaturated base IV was prepared by reduction of II with sodium in alcohol, following essentially the procedure described by Matter, except that the resultant mixture of III and IV was separated by fractional crystallization of the hydrobromides, instead of the hydrochlorides, from acetone. The two end fractions had melting points of 246–247 °C. (more soluble) and 243–244 °C. respectively. The more soluble fraction was identical with the hydrobromide of III obtained by catalytic reduction. From the less soluble fraction, a base IV was regenerated, b.p. 155–157 °C./760 mm. and n_D^{25} 1.4562. From it were prepared:

The hydrochloride of IV, from absolute alcohol, m.p. 232–233 °C. Matter reports 232–3 °C.

The picrate of IV, orange crystals from benzene, m.p. 161–162 °C. Matter reports 160–161 °C.

Phenylurea of IV, by reaction with phenyl isocyanate in light petroleum, and recrystallized from benzene-light petroleum, m.p. 108–109 °C. (Found: C, 74.4; H, 8.5; N, 10.7%. Calc. for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}$: C, 74.4; H, 8.5; N, 10.8%).

(h) *Grignard Synthesis of IV.*—2,2,6-Trimethyl-4-piperidone was prepared by a modification of the method of King, Mason, and Schryver (1916), by heating diacetoneamine hydrogen oxalate with 100% excess of diethyl acetal in methyl cellosolve under reflux for 4 hr.; the resulting neutral oxalate (72% yield) was decomposed with potassium hydroxide, and the free base recovered by repeated extraction with chloroform.

To a Grignard reagent prepared from magnesium (12 g.) and methyl iodide (70 g.) in dry ether (150 ml.) was added over a period of 1 hr. a solution of 2,2,6-trimethyl-4-piperidone (35 g.) in ether (300 ml.) with stirring, under nitrogen. The mixture was then refluxed for a further hour, decomposed with ice and hydrochloric acid, and the carbinol base liberated from the aqueous solution with sodium hydroxide. After extraction with ether and distillation, it was obtained as a colourless, viscous liquid of b.p. 89–90 °C./10 mm. Yield 24 g., 60%. It was dehydrated by heating for 5 hr. at 100 °C. with a small excess of 50% sulphuric acid; 14 g. of unsaturated base, b.p. 47–48 °C./12 mm., and n_D^{25} 1.4560 was obtained. This base gave derivatives identical with those described above for IV prepared by sodium reduction.

In contrast to Matter's experience, it was not found necessary to carry out the Grignard reaction at –20 °C. (cf. Badger, Cook, and McDonald 1950).

III. ACKNOWLEDGMENT

The author is indebted to Dr. H. H. Hatt for helpful discussion during the course of this work.

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SELF-CONDENSATION REACTIONS OF CHLOROALKYL SULPHIDES

By W. DAVIES* and A. N. HAMBLY*

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Summary

The identity of the product formed by the reaction of 2,2'-dichlorodiethyl sulphide with potassium cyanide has been established by the synthesis of ethylene bis-2-carboxyethyl sulphide and its methyl ester. The preparation of bischloromethyl sulphide has been improved and bischloromethyl disulphide prepared as a by-product. Bischloromethyl sulphide undergoes a self-condensation action when heated with methanolic potassium cyanide solution.

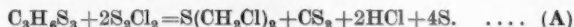
I. INTRODUCTION

The interaction of 2,2'-dichlorodiethyl sulphide (mustard gas) (I) and ethanolic potassium cyanide gave a dinitrile $C_8H_{12}N_2S_2$, which was converted by hydrolysis into a dicarboxylic acid $C_8H_{14}O_4S_2$ (Davies 1920). The structures II and III, which were respectively suggested for these compounds, have now been shown to be correct. The acid III has been synthesized by the condensation of dithioethylene glycol with methyl 2-chloropropionate followed by hydrolysis of the resulting ester.

II. DISCUSSION

The explanation of the conversion of I into II due to Bell, Bennett, and Hock (1927) is essentially the dimerization of I to give the sulphonium type IV. In the presence of potassium cyanide two of the chlorine atoms in the square brackets are replaced by CN groups, and II is formed with loss of ethylene dichloride. This type of change was proved by the conversion of pure I by heat into dithian V and ethylene chloride, and also by the reversal of this process.

In view of the unusual reaction between mustard gas and potassium cyanide, the interaction has been studied of potassium cyanide and the lower homologue of mustard gas, bischloromethyl sulphide (VIII). This was first prepared from the interaction of trithioformaldehyde and sulphur monochloride by Bloch and Höhn (1922) who claimed the reaction to be



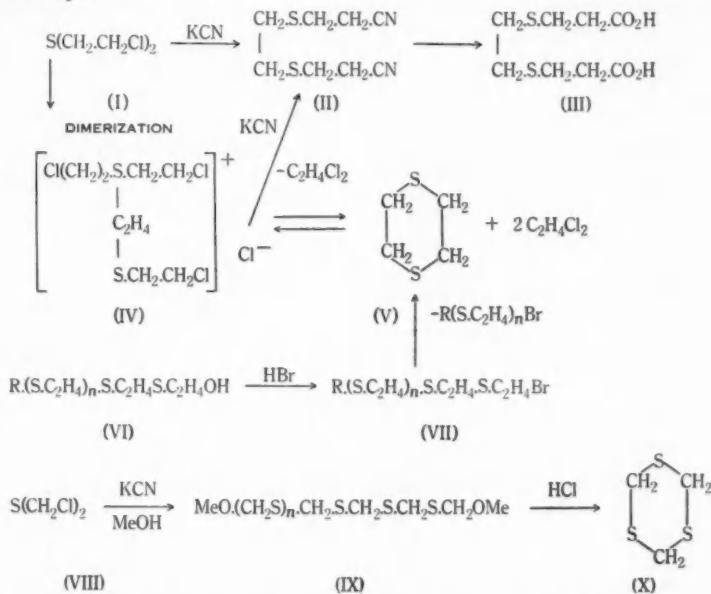
However, when the trithioformaldehyde is perfectly dry the vigorous reaction mentioned by Bloch and Höhn does not occur (also see Mann and Pope 1923), and little hydrogen chloride is evolved. Moreover, when the ratio of trithioformaldehyde to sulphur chloride is higher than that required by equation (A), yields in excess of 120 per cent. of the predicted amount of bischloromethyl

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sulphide, based on the sulphur chloride used, have now been obtained. Hence the reaction may be represented as being to a considerable extent



Other reactions occur, as shown by the isolation of bischloromethyl disulphide, $\text{ClCH}_2\text{S.S.CH}_2\text{Cl}$, in about 10 per cent. yield. This yellow, pungent lachrymatory liquid is a mild skin irritant but not a vesicant. Its probable precursor in the reaction, chloromethyl sulphenyl chloride, ClCH_2SCl , has not been isolated, though the analogous chloromethyl selenyl chloride as well as bischloromethyl selenide and bischloromethyl diselenide are formed (Bridger and Pittman 1950) from the action of chlorine or selenium monochloride on polymeric selenoformaldehyde.



The interaction of bischloromethyl sulphide (VIII) and methanolic potassium cyanide gives polymeric material. The high sulphur content (62.8 per cent.) of even the most soluble material is approaching that of trithioformaldehyde (69.6 per cent.), into which the polymer is largely transformed by the action of concentrated hydrochloric acid. Since Farnworth and Speakman (1949) have shown that fission of disulphide bonds is readily effected by cyanides, it is most unlikely that the polymer contains disulphide links, and hence the analysis indicates many $-S.CH_2-$ groups and that the polymer is of type IX. Though no nitrile analogous to II was derived from VIII, some products of this and I are comparable. Thus, it is known that when halogen-free "polymeric ethylene sulphides" of type VI, easily obtained from I, are heated with hydrogen bromide, they are converted into the six-membered heterocycle, dithian V (Bell, Bennett,

and Hock 1927, p. 1807). This recalls the conversion, by hydrochloric acid of the halogen-free "polymeric methylene sulphide" (IX) into the six-membered heterocycle trithioformaldehyde (X). It is, however, surprising that VIII is recovered unchanged when heated alone in a sealed tube at 200–220 °C. for 8 hr., since I yields dithian V at lower temperatures and even at room temperatures over a long period.

As might be expected, the strongly basic nature of the nitrogen in 2-chloro-alkylamines such as "nitrogen mustard", methyldi-(2-chloroethyl)amine, causes rapid self-condensation (Hanby and Rydon 1947) and in fact, this is faster than with mustard gas. This latter, however, is relatively reactive when compared to its oxygen analogues which seem to be quite inert. For example, 1,2'-dichlorodiethyl ether yields no dioxan when heated at 180–200 °C. for 22 hr., and 1,2'-diiododiethyl ether is unchanged when heated at 100 °C. for 18 hr., though extensive decomposition occurs at 140 °C.

III. EXPERIMENTAL

The synthesis first attempted was that of II by the condensation of ethanolic potassium cyanide with ethylene bis-2-chloroethyl sulphide, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$, made by excess of thionyl chloride on the corresponding glycol, $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$, which was kindly supplied by Dr. G. M. Bennett. However, instead of II the only crystalline material obtained consisted of colourless long thin plates, m.p. about 117 °C., in quantity insufficient for analysis.

(a) *Ethylene Bis-2-carbomethoxyethyl Sulphide*.—(i) Methyl-2-chloropropionate, b.p. 71–73 °C./4 mm. was made in 98% yield by esterification, using hydrogen chloride as catalyst, and in its solution water and not alkali (to which it is very sensitive) was used to remove the hydrochloric acid. Dithioethylene glycol (4.5 g.) was heated in an oxygen-free atmosphere with sodium methylate (2.3 g. Na) and methyl 2-chloropropionate (12.25 g.) in 65 ml. of methanol. After boiling for 4 hr. the solution, which was almost neutral, was poured into water, the oil extracted with ether and the ether solution dried over anhydrous MgSO_4 . After removal of the ether, the residue distilled almost completely at 175–180 °C./0.5 mm., m.p. 29–30 °C. The product, m.p. 29–30 °C. (10 g., 79%) has b.p. 177 °C./0.5 mm. and pure ethylene bis-2-carbomethoxyethyl sulphide crystallizes from light petroleum (b.p. 40–50 °C.) in thick plates, m.p. 29.5–30.5 °C.; n_D^{21} 1.5062 (Found: S, 24.5%; mol. wt. (Rast), 272. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$: S, 24.1%; mol. wt., 266).

(ii) The acid from the hydrolysis of the nitrile (Davies 1920) was esterified with methanol (HCl) and the product when recrystallized from light petroleum had n_D^{21} 1.5065 and did not depress the m.p. of ethylene bis-2-carbomethoxyethyl sulphide.

(b) *Ethylene Bis-2-carboxyethyl Sulphide*.—Saponification of the esters prepared by methods (i) and (ii) followed by acidification, gave the corresponding acid as pearly leaves which after repeated solution in alkali and reprecipitation had m.p. 156–159 °C. and 155–158 °C. respectively (cf. Davies 1920). The m.p. was not depressed by admixture (Found: equiv. wt. by titration, 120. Calc. for $\text{C}_8\text{H}_{14}\text{O}_4\text{S}_2$: equiv. wt., 119).

(c) *Bischloromethyl Sulphide*.—Well-dried trithioformaldehyde, m.p. 215–216 °C./320 g. was heated with sulphur monochloride (420 g.; 250 ml.) for 2 hr. on a water-bath. No trouble was experienced in controlling the reaction even with these quantities (contrast Bloch and Höhn 1922). The mixture was then distilled under reduced pressure until decomposition commenced; 304 g. of pale yellow distillate was obtained. The residue was an amber coloured resin. The crude distillate when redistilled through a Vigreux column gave bischloromethyl sulphide, 211 g., b.p. 52–55 °C./14 mm. and bischloromethyl disulphide, 17 g., b.p. 96.5–99.5 °C./14 mm. A further 39 g. of $\text{S}(\text{CH}_2\text{Cl})_2$ and 8 g. of $\text{S}_2(\text{CH}_2\text{Cl})_2$ were recovered from the intermediate fractions.

Bischloromethyl disulphide has b.p. 98.5–99.5 °C./15 mm., n_D^{17} 1.5894 (Found: S, 39.0; Cl, 43.4%; mol. wt. (cryoscopic in C_6H_6), 163. Calc. for $C_2H_4Cl_2S_2$: S, 39.3; Cl, 43.5%; mol. wt., 163).

(d) *Reaction of Bischloromethyl Sulphide in Presence of Potassium Cyanide.*—Bischloromethyl sulphide (20 g.) was added to potassium cyanide (20 g.) in boiling methanol (170 ml.), the boiling was continued for 10 min. and then the mixture was poured into a large volume of cold water. The dried curd from three such preparations weighed 16.5 g. This was extracted with two portions of 250 ml. of light petroleum (b.p. 100–120 °C.) and from the cold extract 5.7 g. of a solid with a pearly sheen, m.p. 86–90 °C., was obtained. This chlorine and nitrogen-free material gave analytical values corresponding to $C_{10}H_{22}O_2S_3$ (Found: C, 25.9; H, 4.7; S, 62.8%; mol. wt. (Rast), 445. Calc. for $C_{10}H_{22}O_2S_3$: C, 26.0; H, 4.8; S, 62.4%; mol. wt., 462). This substance, however, is not a pure compound, but the more soluble portion of a complex mixture of polymers. Hydroxy groups seem to be absent for the solid (on this occasion melting at 90–112 °C.) obtained by prolonged extraction with light petroleum gave no methane with methyl magnesium iodide in anisole.

(e) *Reaction of Condensation Product with Hydrochloric Acid.*—The crystalline product from the previous action (0.5 g.) was added to concentrated hydrochloric acid (5 ml.) and evaporated to dryness on the water-bath. Treatment with a similar quantity of acid was repeated twice and the residue was then extracted with boiling, glacial acetic acid. From this extract crystalline needles of trithioformaldehyde separated which had m.p. and mixed m.p. with an authentic sample 215–216 °C.

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STUDIES ON THE LIGNIN OF *EUCALYPTUS REGNANS* F. MUELL.

VII. THE ACID HYDROLYSIS OF ETHANOL LIGNIN-A

By J. W. T. MEREWETHER*

[Manuscript received November 12, 1952]

Summary

Ethanol lignin-A from the ethanolysis of *Eucalyptus regnans* F. Muell. has been hydrolysed with dilute hydrochloric acid with the object of ascertaining whether the combined ethoxyl is present as an acetal or as ether. Hydrolysis with 12 per cent. hydrochloric acid was found to split off one ethoxyl group, while hydrolysis with 20 per cent. acid brought about complete de-ethylation. The de-ethylated ethanol lignin-A contained one carbonyl group less and two hydroxyl groups more than the original ethanol lignin-A. These results lend no support to the hypothesis that alcohol lignins are acetals, and favour the theory that the combined alkoxy is probably present as ether.

I. INTRODUCTION

When wood meal is treated with an alcohol in the presence of a catalyst, the greater part of the lignin reacts with the alcohol to yield an alcohol-soluble derivative. Some of the alcohol condenses with the lignin, and it has been found (Merewether 1953) that the main reaction product from the ethanolysis of *Eucalyptus regnans* F. Muell., ethanol lignin-A, contained combined ethoxyl in the proportion of two ethoxyls to nine methoxyls. The nature of the reaction involved is not yet clear, and there are contradictions in the literature. For example, Friedrich and Diwald (1925) claimed that their ethanol spruce lignin lost alkoxy when treated with warm 2N sodium hydroxide, and became soluble in sodium carbonate. Later Friedrich (1928) extended this work to a study of the methanolysis of spruce, finding that two additional methoxyls were introduced; of these, one could be removed by alkaline hydrolysis, and was therefore present as an ester. King and Hibbert (1935) were unable to confirm these findings, both ethanol and methanol spruce lignin being unaffected by 10 per cent. sodium hydroxide. Holmberg and Runius (1925) also found ethanol lignin to be unaffected by boiling aqueous potassium hydroxide, and concluded that it was very probably an acetal.

The stability of ethanol lignin to alkaline hydrolysis was confirmed by Hägglund and Urban (1928), who had earlier (1927) shown that the alcoholysis reaction worked just as well with *isobutyl* and *isoamyl* alcohols, agreeing with Holmberg's theory that alcohol lignins were acetals. Subsequently Hägglund, Johnson, and Trygg (1930) treated a solution of pentanol lignin in glacial acetic acid with 25 per cent. sulphuric acid for 1 hr. on the water-bath, and reduced the

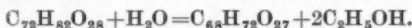
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pentoxy content from 15.9 to 3.1 per cent. Using 1 per cent. hydrochloric acid, the pentoxy content was reduced to 7.4 per cent. after 7 hr. They regarded this as convincing proof of the acetal theory.

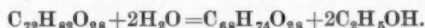
In a paper on methanol lignin, Brauns and Hibbert (1935) queried this conclusion. Later Brauns (1939) showed that 72 per cent. sulphuric acid will split off the introduced methoxy from methanol native lignin, and the same reagent was used by Charbonnier (1942) to split off the butoxy from butanol lignin. Both these workers subscribed to the acetal theory.

There is a third possibility, that alcohol lignins are neither esters nor acetals, but ethers. Holmberg (1935) has found that α -phenylethyl alcohol is converted to its ethyl ether by ethanolic hydrogen chloride, and has suggested that the alcoholysis of lignin may involve the etherification of a side-chain alcoholic hydroxyl of this nature. In support of this hypothesis it is well known that compounds such as α -ethoxypropiovanillone have been isolated as by-products of the ethanolysis reaction (Cramer, Hunter, and Hibbert 1939). Freudenberg (1939) has suggested that such a reaction may be preceded by the opening of an oxygen ring to yield side-chain ketols, which are then etherified. The inability of Hägglund, Johnson, and Trygg (1930) to obtain complete removal of introduced alkoxy would be more readily explained by the ether theory.

The data obtained for *E. regnans* ethanol lignin-A agreed well with the empirical formula $C_{72}H_{82}O_{28}$ containing nine methoxy and two ethoxy groups. If this were an acetal it should be readily hydrolysed by dilute mineral acids according to the equation :



If, on the other hand, the ethoxy groups are present as ethers, the ethanol lignin should hydrolyse less readily, and according to the equation :



To distinguish between these two alternatives by elementary analysis would be well-nigh impossible. But, on the assumption that no other changes take place, it should be possible by group determination to differentiate between the product of hydrolysis of an acetal and that of a di-ether. The former will yield a product with an additional carbonyl group and no additional hydroxyls, or perhaps one more if the new carbonyl enolizes, while the latter will yield a product with no additional carbonyl, but two additional hydroxyls.

When ethanol lignin-A was refluxed for 6 hr. with 12 per cent. hydrochloric acid, partial de-ethylation took place, the total alkoxy content being reduced from 24.6 to 22.1 per cent. (methoxy content 20.7 per cent.). This corresponds to the replacement of one ethoxy group by a hydroxyl. A further 8 hr. refluxing had no effect, yielding a product with unchanged total alkoxy (22.3 per cent.).

This partially de-ethylated product was then slowly distilled with 12 per cent. hydrochloric acid for 2 hr., the concentration of the acid gradually rising to that of constant boiling hydrochloric acid. This resulted in complete de-ethylation, the total alkoxy content (20.4 per cent.) being the same as the methoxy content (20.8 per cent.). That the elimination of ethoxy had been complete was confirmed by a C-methyl determination. Ethanol lignin-A

contained 3.4 per cent. C-methyl, corresponding to two ethoxyl groups and one terminal methyl (*E. regnans* methanol lignin-A contains 0.6 per cent. C-methyl, corresponding to one terminal methyl group). The C-methyl content of the de-ethylated ethanol lignin-A was 0.8 per cent., corresponding to one terminal methyl group.

Similar results were obtained when ethanol lignin-A was de-ethylated by this method, the product containing 20.7 per cent. total alkoxy, 20.8 per cent. methoxy, and 1.3 per cent. C-methyl.

On methylation with diazomethane ethanol lignin-A yields a dimethyl derivative. Methylation of de-ethylated ethanol lignin-A with diazomethane yields a trimethyl derivative, indicating that one new acidic hydroxyl group has been formed. Acetylation of ethanol lignin-A with acetic anhydride in pyridine yields a hepta-acetate. Under the same conditions the de-ethylated product also yielded a hepta-acetate. On the other hand, benzoyl chloride in pyridine, which yielded a heptabenzoate with ethanol lignin-A, when applied to de-ethylated ethanol lignin-A, yielded a product which was unequivocally a nonabenzoate.

In order to determine the carbonyl group content the de-ethylated ethanol lignin-A was treated with both phenylhydrazine and *p*-nitrophenylhydrazine. It has been found with other lignin preparations from *E. regnans* that satisfactory conditions for hydrazone formation are to carry out the reaction in boiling glacial acetic acid. Using these conditions with a de-ethylated ethanol lignin-A, a low yield of a partially resinified product was obtained, the product was difficult to purify, and anomalous analyses were found. Finally, it was found satisfactory to carry out the reaction in boiling dioxan, using a column fitted with a total-condensation variable take-off head to remove any water formed in the reaction. The results were surprising. Ethanol lignin-A has two carbonyl groups, yielding bisphenylhydrazones; the de-ethylated ethanol lignin yielded monophenylhydrazones. These data are summarized in Table 1.

The first conclusion to be drawn is that the acid hydrolysis has completely split off the two ethoxyl groups. The second is that some other change has occurred, in that the carbonyl content, instead of increasing as it would if ethanol lignin were an acetal, or remaining constant in the case of ether-fission, has been halved. Thirdly, the number of hydroxyl groups capable of reacting with benzoyl chloride in pyridine has increased by two.

Had this increase been unaccompanied by any other changes it could have been regarded as proof that the ethoxyl in ethanol lignin-A was ether ethoxyl. As it is there is the possibility that the two new hydroxyls have resulted from some change other than ether-fission.

Nevertheless the facts established are more in favour of the ether theory than the acetal. One would expect an acetal to be readily hydrolysed by 12 per cent. hydrochloric acid, and the fact that only half the ethoxyl was split off by this treatment would be hard to explain for an acetal. Secondly, the absence of any increase in carbonyl content, coupled with the formation of two new hydroxyl groups, lends more support to the ether than to the acetal theory.

TABLE I
DE-ETHYLATED ETHANOL LIGNIN-A

No.	Compound	Empirical Formula	Constituent Groups		C (%)	H (%)	N (%)	OCH ₃		COCH ₃ (%)
			OCH ₃	OH Acyl				(a) (%)	(b) (%)	
1	De-ethylated ethanol lignin-A	C ₉₈ H ₇₄ O ₂₈ = 1339	9	9 0	f. 61.3 c. 61.0	5.5 5.6	—	20.7 20.9	20.8	—
2	1+CH ₃ N ₃	C ₇₁ H ₅₉ O ₁₈ = 1381	12	6 0	f. 61.9 c. 61.7	5.7 5.8	—	27.1 27.0	27.0	—
3	1+Ac ₂ O	C ₉₂ H ₈₃ O ₃₁ = 1634	9	2 7	f. 60.4 c. 60.3	5.5 5.4	—	17.5 17.1	17.1	19.0 18.5
4	1+BzCl	C ₁₃₁ H ₁₁₀ O ₃₇ = 2276	9	0 9	f. 69.2 c. 69.1	4.8 4.9	—	12.5 12.3	—	—
5	1+Ph.NH.NH ₂	C ₇₇ H ₅₈ O ₂₇ N ₁ = 1429	9	— —	f. 62.8 c. 62.2	5.6 5.6	2.2 2.0	19.7 19.6	—	—
6	1+p-NO ₂ -C ₆ H ₄ .NH.NH ₂	C ₉₄ H ₇₉ O ₃₃ N ₃ = 1474	9	— —	f. 60.1 c. 60.3	5.4 5.4	2.9 2.9	18.8 19.0	—	—

(a) Total alkoxy! by the method of Viebock and Brecher.

(b) Methoxy! by the method of Willstätter and Utzinger.

Summing up, it can be said that, while no rigid proof is adduced, the new facts support the theory that the ethoxyl introduced by ethanolysis is ether rather than acetal in nature.

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *De-ethylated Ethanol Lignin-A*.—Ethanol lignin-A (16 g.), prepared as previously described (Merewether 1953), was refluxed with 12% hydrochloric acid for 6 hr. The residue (15.0 g.) was purified once from dioxan-ether (yield 13.0 g.) and separated into an acetone-insoluble fraction, which was purified once from dioxan-ether (yield 3.2 g.), and an acetone-soluble fraction which was isolated from water (yield 9.0 g.) and then purified three times from dioxan-ether (yield 7.9 g.) (Found: acetone-insoluble, 23.9% total alkoxy; acetone-soluble, 22.1% total alkoxy).

The two fractions were then combined and refluxed with 12% hydrochloric acid for a further 8 hr., and separated as above (Found: acetone-soluble fraction, 22.3% total alkoxy).

The two fractions were again combined, and distilled with 12% hydrochloric acid for 2 hr. By this means the concentration of acid was gradually increased, and the ethanol was removed as it was liberated. The residue was filtered off and separated as above into acetone-insoluble (2.1 g.) and acetone-soluble (5.5 g.) (Found for acetone-insoluble fraction: C, 61.9; H, 5.5; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 21.7%; Found for acetone-soluble fraction: C, 61.3; H, 5.5; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 20.4; OCH_3 , 20.8%; $(\text{C})\text{CH}_3$, 0.8%. Calc. for $\text{C}_{48}\text{H}_{74}\text{O}_{28}$ (1339): C, 61.0; H, 5.6; OCH_3 , 20.9; $(\text{C})\text{CH}_3$, 1.1%. Found for the acetone-soluble fraction obtained by a single stage de-ethylation of ethanol lignin-A by these means: C, 61.3; H, 5.4; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 20.7; OCH_3 , 20.8; $(\text{C})\text{CH}_3$, 1.3%). De-ethylated ethanol lignin-A is a dark brown amorphous solid with no sharp melting point. The softening or decomposition temperature was extremely difficult to determine, but appeared to be about 210 °C. It is soluble in acetone, acetic acid, ethyl acetate, dioxan, pyridine, and aqueous sodium hydroxide, slightly soluble in ethanol and chloroform, and insoluble in ether, light petroleum, benzene, water, and aqueous sodium bicarbonate.

(b) *Trimethyl De-ethylated Ethanol Lignin-A*.—De-ethylated ethanol lignin-A (6 g.) in dioxan (60 cc.) was allowed to react for 48 hr. at room temperature with a dioxan solution of diazomethane from nitrosomethylurea (10 g.). The solution was then concentrated down to about 60 cc. and remethylated under the same conditions. It was then concentrated again to about 60 cc., the product isolated by precipitation from ether (600 cc.) and purified twice from dioxan-ether. Yield 5.0 g. (Found: C, 61.9; H, 5.7; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 27.1; OCH_3 , 27.0%. Calc. for $\text{C}_{71}\text{H}_{98}\text{O}_{28}$ (1381): C, 61.7; H, 5.8; OCH_3 , 27.0%).

(c) *De-ethylated Ethanol Lignin-A Hepta-acetate*.—De-ethylated ethanol lignin-A (2 g.) in pyridine (20 cc.) was treated with acetic anhydride (6 cc.) for 48 hr. at room temperature. The product was isolated from ether and purified twice from dioxan-ether. Yield 1.7 g. (Found: C, 60.4; H, 5.5; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 17.5; OCH_3 , 17.1; COCH_3 , 19.0%. Calc. for $\text{C}_{88}\text{H}_{108}\text{O}_{35}$ (1634): C, 60.3; H, 5.4; OCH_3 , 17.1; COCH_3 , 18.5%). De-ethylated ethanol lignin-A hepta-acetate is a brown solid softening at 214 °C. and is soluble in the same solvents as de-ethylated ethanol lignin-A except that it is insoluble in ethanol and cold dilute aqueous sodium hydroxide.

(d) *De-ethylated Ethanol Lignin-A Nonabenzoate*.—De-ethylated ethanol lignin-A (1 g.) in pyridine (10 cc.) was treated with benzoyl chloride (3 cc.) for 48 hr. at room temperature. The product was worked up in the usual manner (for example, Merewether 1953) and purified three times from chloroform-ether. Yield 0.5 g. (Found: C, 69.2; H, 4.8; OCH_3 , 12.5%. Calc. for $\text{C}_{131}\text{H}_{119}\text{O}_{27}$ (2276): C, 69.1; H, 4.9; OCH_3 , 12.3%). De-ethylated ethanol lignin-A nonabenzoate is a brown solid softening at 208 °C. It is soluble in acetone, chloroform, benzene, dioxan, and pyridine, slightly soluble in ethanol and ethyl acetate, and insoluble in acetic acid, ether, light petroleum, water, and dilute aqueous sodium hydroxide.

(e) *De-ethylated Ethanol Lignin-A Phenylhydrazone*.—De-ethylated ethanol lignin-A (2 g.), redistilled phenylhydrazine (2 cc.), and anhydrous dioxan (150 cc.) were refluxed under a column

fitted with a total-condensation variable take-off head (Quickfit and Quartz Cat. No. FC. 15/13) for 2 hr., the condensate in the trap being periodically removed. The mixture was then concentrated to about 20 cc., and the product isolated from ether (200 cc.). Yield 1.8 g. (Found: C, 62.8; H, 5.6; N, 2.2; OCH_3 , 19.7%. Calc. for $\text{C}_{74}\text{H}_{80}\text{O}_{27}\text{N}_2$ (1329): C, 62.2; H, 5.6; N, 2.0; OCH_3 , 19.6%). De-ethylated ethanol lignin-A phenylhydrazone is a brown powder softening at 145 °C., soluble in acetone, chloroform, acetic acid, dioxan, pyridine, and aqueous sodium hydroxide, slightly soluble in ethanol and ethyl acetate, and insoluble in ether, light petroleum, benzene, and water.

(f) *De-ethylated Ethanol Lignin-A p-Nitrophenylhydrazone*.—De-ethylated ethanol lignin-A (2 g.) was treated with *p*-nitrophenylhydrazine under conditions identical with those described for the foregoing preparation. Yield 1.8 g. (Found: C, 60.1; H, 5.4; N, 2.9; OCH_3 , 18.8%. Calc. for $\text{C}_{74}\text{H}_{78}\text{O}_{29}\text{N}_4$ (1474): C, 60.3; H, 5.4; N, 2.9; OCH_3 , 19.0%). De-ethylated ethanol lignin-A *p*-nitrophenylhydrazone is an orange-brown powder softening at 190 °C., and is soluble in the same solvents as the phenylhydrazone and it is also soluble in ethyl acetate.

III. ACKNOWLEDGMENTS

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STUDIES ON THE LIGNIN OF *EUCALYPTUS REGNANS* F. MUELL.

VIII. THE ISOLATION OF AN ETHER-SOLUBLE ETHANOL LIGNIN

By J. W. T. MEREWETHER*

[Manuscript received January 16, 1953]

Summary

A second fraction, soluble in ether, has been isolated from the products of ethanolysis of *Eucalyptus regnans* F. Muell. wood meal. This fraction, designated ethanol lignin-B, has been characterized by methylation with diazomethane, acetylation and benzylation both of the ethanol lignin-B and its methyl derivative, and the formation of a phenylhydrazone. The analysis of these derivatives indicates that, while ethanol lignin-B is very similar to the previously described ether-insoluble ethanol lignin-A, it differs in its reaction with benzoyl chloride and with phenylhydrazone.

I. INTRODUCTION

It is well known that when wood meal is treated with an alcohol in the presence of a catalyst, the lignin reacts with the alcohol to yield a mixture of condensation products, alcohol lignins, and it has been shown (Patterson *et al.* 1941) that these may be separated by fractional precipitation. In a recent paper (Merewether 1953) it was shown that the main product from the ethanolysis of *Eucalyptus regnans* F. Muell. is an ether-insoluble derivative, ethanol lignin-A. During the isolation and purification of this product a second fraction, soluble in ether, was obtained and designated ethanol lignin-B, and this paper deals with the properties of this ether-soluble fraction.

A series of six derivatives was made, and in Table 1 are set out the analytical values obtained, the corresponding data for ethanol lignin-A being included for comparison. While ethanol lignin-B is obviously different from ethanol lignin-A, in so far as its colour is different, its softening point is some 70 °C. lower, and it is soluble in solvents in which ethanol lignin-A is insoluble, it is interesting to note that its chemical analysis is almost identical with that of ethanol lignin-A.

The ratio of nine methoxyl to two ethoxyl groups found for ethanol lignin-A is also found here for ethanol lignin-B, and in the first five compounds the alkoxy values are identical for the two fractions, indicating a very similar structure. The main differences occur in their reaction with benzoyl chloride and with phenylhydrazine. In the former reaction, the benzylation of diazomethane methylated ethanol lignin-A yielded a product with the alkoxy content of a pentabenzoylate, while the B fraction yields a tetrabenzoylate. With phenylhydrazine, ethanol lignin-A yielded a bisphenylhydrazone, while the higher alkoxy and the lower nitrogen values obtained with the B fraction indicate the formation of a monophenylhydrazone. Finally, the slight but regular drop in

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TABLE 1
COMPARISON OF ETHANOL LIGNIN-A AND ETHANOL LIGNIN-B

No.	Compound	Fraction	C (%)	H (%)	N (%)	OR (%)	OCH ₃ (%)
1	Ethanol lignin	A	62.3	5.9	—	24.6	20.0
		B	61.6	5.9	—	24.7	20.2
2	1 + CH ₂ N ₂	A	62.5	6.2	—	28.3	23.8
		B	62.4	6.1	—	28.8	24.1
3	1 + Ac ₂ O	A	61.3	5.7	—	20.3	16.5
		B	60.9	5.7	—	20.0	16.8
4	2 + Ac ₂ O	A	62.0	5.8	—	24.6	21.0
		B	61.3	5.9	—	24.7	21.0
5	1 + BzCl	A	68.4	5.3	—	16.2	13.1
		B	68.3	5.1	—	15.9	13.4
6	2 + BzCl	A	65.8	5.5	—	20.6	17.8
		B	66.4	5.6	—	22.2	19.1
7	1 + Ph.NH.NH ₂	A	64.4	6.0	3.5	21.6	17.7
		B	63.1	5.9	2.5	23.3	19.3

TABLE 2
ETHANOL LIGNIN-B

No.	Compound	Empirical Formula	Constituent Groups				C (%)	H (%)	N (%)	OR (%)	OCH ₃ (%)
			OEt	OMe	OH	Acyl					
1	Ethanol lignin-B	C ₇₁ H ₈₉ O ₂₈ = 1381	2	9	7	0	f. 61.6	5.9	—	24.7	20.2
							c. 61.7	5.8	—	24.7	20.2
2	1 + CH ₂ N ₂	C ₇₃ H ₈₄ O ₂₈ = 1409	2	11	5	0	f. 62.4	6.1	—	28.8	24.1
							c. 62.3	6.0	—	28.6	24.2
3	1 + Ac ₂ O	C ₈₅ H ₉₈ O ₃₅ = 1672	2	9	0	7	f. 60.9	5.7	—	20.0	16.8
							c. 61.0	5.7	—	20.4	16.7
4	2 + Ac ₂ O	C ₈₃ H ₉₈ O ₃₃ = 1620	2	11	0	5	f. 61.3	5.9	—	24.7	21.0
							c. 61.5	5.9	—	24.9	21.1
5	1 + BzCl	C ₁₃₀ H ₁₀₉ O ₃₅ = 2110	2	9	0	7	f. 68.4	5.1	—	15.9	13.4
							c. 68.3	5.2	—	16.1	13.2
6	2 + BzCl	C ₁₀₁ H ₁₀₀ O ₃₂ = 1826	2	11	1	4	f. 66.4	5.6	—	22.2	19.1
							c. 66.4	5.5	—	22.0	18.6
7	1 + Ph.NH.NH ₂	C ₇₇ H ₈₆ O ₂₇ N ₂ = 1472	2	9	—	—	f. 63.1	5.9	2.5	23.3	19.3
							c. 62.8	5.9	1.9	23.2	19.0

the carbon analysis of the *B* fraction relative to the *A* fraction suggests a slightly lower carbon content in the former.

The formula $C_{72}H_{82}O_{28}$ with nine methoxyls, two ethoxyls, and seven hydroxyls was found to agree with the data obtained for ethanol lignin-A, and in Table 2 are set out the results obtained with ethanol lignin-B, compared with the values calculated for $C_{71}H_{80}O_{28}$ and the same substituent groups.

II. EXPERIMENTAL

Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Dimethyl Ethanol Lignin-B*.—Ethanol lignin-B (10 g.), prepared as previously described (Merewether 1953) in dioxan (100 cc.), was treated with a dioxan solution of diazomethane from the alkaline decomposition of nitrosomethylurea (5 g.). After standing at room temperature for 48 hr. the solution was concentrated to about 100 cc. and remethylated under the same conditions. After a third methylation the solution was concentrated to about 100 cc. and added dropwise to vigorously stirred anhydrous ether (1 l.). The precipitate was filtered off and discarded, and the filtrate was added to an equal volume of light petroleum (30–50 °C.). The precipitate was filtered off, washed with light petroleum and dried, and purified twice by dissolving in chloroform, adding the solution to 10 volumes of ether to remove any traces of ether-insoluble material, and precipitating the product from an equal volume of light petroleum. Yield 5.0 g. (Found: C, 62.4; H, 6.1; $OCH_3 + OC_2H_5$ as OCH_3 , 28.8; OCH_3 , 24.1%. Calc. for $C_{72}H_{82}O_{28}$ (1409): C, 62.3; H, 6.0; $OCH_3 + OC_2H_5$ as OCH_3 , 28.6; OCH_3 , 24.2%). Dimethyl ethanol lignin-B is a yellow powder softening at 122 °C., is soluble in ethanol, acetone, chloroform, acetic acid, ethyl acetate, benzene, dioxan, and pyridine, slightly soluble in ether, and insoluble in light petroleum, water, and dilute alkalis.

(b) *Hepta-acetyl Ethanol Lignin-B*.—Ethanol lignin-B (1.5 g.) in pyridine (15 cc.) was treated with acetic anhydride (5 cc.) for 48 hr. at room temperature. The product was isolated as above from ether and light petroleum, and purified twice from dioxan-ether-light petroleum. Yield 0.8 g. (Found: C, 60.9; H, 5.7; $OCH_3 + OC_2H_5$ as OCH_3 , 20.0; OCH_3 , 16.8%. Calc. for $C_{88}H_{84}O_{35}$ (1672): C, 61.0; H, 5.7; $OCH_3 + OC_2H_5$ as OCH_3 , 20.4; OCH_3 , 16.7%). Hepta-acetyl ethanol lignin-B is a pale cream powder softening at 136 °C., and is soluble in the same solvents as dimethyl ethanol lignin-B.

(c) *Penta-acetyldimethyl Ethanol Lignin-B*.—Dimethyl ethanol lignin-B (0.3 g.) in pyridine (3 cc.) was treated with acetic anhydride (1 cc.) and worked up in the same way as the previous preparation. Yield 0.2 g. (Found: C, 61.3; H, 5.9; $OCH_3 + OC_2H_5$ as OCH_3 , 24.7; OCH_3 , 21.0%. Calc. for $C_{88}H_{84}O_{35}$ (1620): C, 61.5; H, 5.9; $OCH_3 + OC_2H_5$ as OCH_3 , 24.9; OCH_3 , 21.1%). Penta-acetyldimethyl ethanol lignin-B is a light buff solid softening at 125 °C., and soluble in the same solvents as dimethyl ethanol lignin-B except that it is only slightly soluble in ethanol.

(d) *Heptabenzoyl Ethanol Lignin-B*.—Ethanol lignin-B (1.5 g.) in pyridine (15 cc.) was treated with benzoyl chloride (4 cc.) and worked up as described for the benzoylation of ethanol lignin-A. Yield 1.7 g. Yield, after three purifications from dioxan-ether-light petroleum, 0.8 g. (Found: C, 68.4; H, 5.1; $OCH_3 + OC_2H_5$ as OCH_3 , 15.9; OCH_3 , 13.4%. Calc. for $C_{100}H_{108}O_{35}$ (2110): C, 68.3; H, 5.2; $OCH_3 + OC_2H_5$ as OCH_3 , 16.1; OCH_3 , 13.2%). Heptabenzoyl ethanol lignin-B is a light brown solid softening at 183 °C., and soluble in the same solvents as penta-acetyldimethyl ethanol lignin-B.

(e) *Tetrabenzoyldimethyl Ethanol Lignin-B*.—Dimethyl ethanol lignin-B (0.3 g.) in pyridine (3 cc.) was treated with benzoyl chloride (1 cc.) and worked up as described for the previous preparation. Yield 0.2 g. (Found: C, 66.4; H, 5.6; $OCH_3 + OC_2H_5$ as OCH_3 , 22.2; OCH_3 , 19.1%. Calc. for $C_{100}H_{108}O_{35}$ (1826): C, 66.4; H, 5.5; $OCH_3 + OC_2H_5$ as OCH_3 , 22.0; OCH_3 , 18.6%). Tetrabenzoyldimethyl ethanol lignin-B is a pale tan solid softening at 125 °C., and is soluble in the same solvents as penta-acetyldimethyl ethanol lignin-B.

(f) *Ethanol Lignin-B Phenylhydrazone*.—Ethanol lignin-B (0.9 g.) in dioxan (70 cc.) was refluxed with phenylhydrazine (1 g.) for 2 hr., using a column fitted with a total-condensation

variable take-off head to remove dioxan-water azeotrope as it formed. The mixture was then concentrated to about 10 cc., and the product precipitated from ether-light petroleum. This was filtered off, and extracted in a Soxhlet for 7 hr. with light petroleum. It was then dissolved in dioxan (10 cc.), the solution added to ether (100 cc.), and the precipitate discarded. The filtrate was added to light petroleum (100 cc.) and the precipitate repurified once more by Soxhlet extraction with light petroleum and precipitation from dioxan-ether-light petroleum. Yield 0.4 g. (Found: C, 63.1; H, 5.9; N, 2.5; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 23.3; OCH_3 , 19.3%. Calc. from $\text{C}_{77}\text{H}_{88}\text{O}_{27}\text{N}_2$ (1472): C, 62.8; H, 5.9; N, 1.9; $\text{OCH}_3 + \text{OC}_2\text{H}_5$ as OCH_3 , 23.2; OCH_3 , 19.0%). Ethanol lignin-B phenylhydrazone is a dull cream coloured solid softening at 163 °C., and is soluble in the same solvents as penta-acetyldimethyl ethanol lignin-B, except that it is soluble in dilute aqueous alkalis.

III. ACKNOWLEDGMENTS

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THE ESSENTIAL OIL OF *MYOPORUM CRASSIFOLIUM* FORST.

By K. G. O'BRIEN,* A. R. PENFOLD,† and R. L. WERNER*

[Manuscript received October 27, 1952]

Summary

The essential oil of *Myoporum crassifolium* Forst., a shrub endemic to New Caledonia, is shown to consist principally of a tertiary sesquiterpene alcohol which is either identical with or isomeric with synthetic bisabolol.

I. INTRODUCTION

The essential oil of *Myoporum crassifolium* Forst. was first examined by Messrs. Plaimar Ltd. (1930), purely in relation to its possible application to the perfumery and essential oil industry. No indication was given as to the nature of the chemical constituents.

In 1941, a sample of the wood was received at the Museum of Applied Arts and Sciences, Sydney, from New Caledonia, where it is known as Anime or Anyne wood, from which the essential oil was obtained by steam distillation. A preliminary investigation indicated that the principal constituent of the oil was probably a sesquiterpene alcohol of high laevorotation.

Further examination of the oil was deferred until 1947 when the investigation was reopened in order to establish the chemical identity of the principal constituent.

Examination of the fractions obtained after repeated fractionation under reduced pressure showed that the majority possessed similar constants, the density, optical rotation, refractive index, and solubility in alcohol (80 per cent.) being notably high in each. The fractions of similar physical properties were mixed. Elementary analysis and molecular weight estimations showed the molecular formula to be $C_{16}H_{26}O$.

Dehydrogenation with platinum/carbon catalyst or sulphur gave hydrocarbons which failed to give picrate derivatives, indicating the possible absence of bi- or tricyclic hydrocarbon skeletons.

On hydrogenation under the conditions of Ruzicka and van Veen (1929) it was found that the equivalent of three molecules of hydrogen was absorbed. Such a phenomenon could not be due to the presence of three double bonds in the alcohol since such a compound would not be capable of forming bisabolene trihydrochloride or trihydrobromide and can conceivably only be due to hydrogenolysis occurring during the hydrogenation. The absorption of three molecules of hydrogen by the hydrocarbon recovered from the trihydrochloride confirms these results and excludes the possibility of the presence of a cyclopropane ring.

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The ease with which the alcohol was dehydrated on treatment with formic acid (100 per cent.) or on azeotropic distillation with benzene in the presence of a little concentrated sulphuric acid, indicated that the hydroxyl group was most likely in the tertiary position. This would account for the lack of derivative formation with the usual alcohol reagents.

The phenylazophenylurethane formed orange needles, m.p. 103–103.5 °C.

The alcohol gave a positive test for unsaturation when treated with bromine in carbon tetrachloride and potassium permanganate in acetone respectively.

On treatment of the alcohol with hydrogen chloride, an optically-inactive crystalline derivative of molecular composition $C_{14}H_{27}Cl_3$, m.p. 79–80 °C., was formed, apparently identical with bisabolene trihydrochloride prepared by

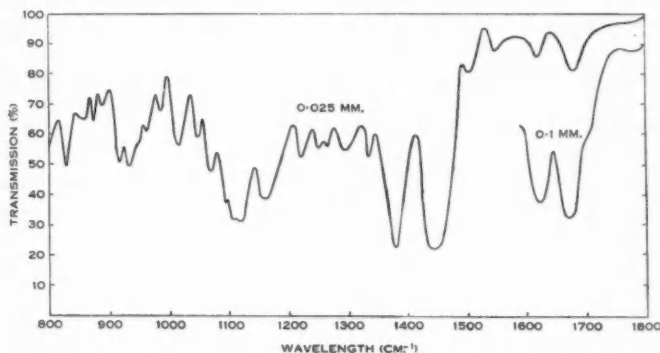


Fig. 1.—The infra-red spectrum of the tertiary alcohol from *M. crassifolium*.

Ruzicka and Liguori (1931), and undepressed in m.p. on mixing with an authentic sample. On treatment of this trihydrochloride with sodium acetate in glacial acetic acid, a hydrocarbon was obtained with physical properties similar to those of bisabolene (cf. Ruzicka and Capato 1925). On treatment of this hydrocarbon with hydrogen chloride, a trihydrochloride was obtained with m.p. 79–80 °C., which was not depressed on mixing with the original trihydrochloride. The hydrocarbon on treatment with hydrogen bromide formed a crystalline trihydrobromide, m.p. 84 °C., identical with that recorded for bisabolene trihydrobromide. It was concluded from these results that the alcohol was a tertiary sesquiterpene alcohol containing two double bonds.

It has previously been demonstrated that isopropylidene and isopropenyl groups give unique infra-red absorption bands which may be used to detect their presence (Thompson and Torkington 1945; Rasmussen and Brattain 1947; Barnard *et al.* (1950). Thus an isopropylidene group gives rise to two characteristic bands, one about 1670 cm^{-1} , due to the stretching of the $C=C$ linkage and the other in the region from 820–840 cm^{-1} due to the out-of-plane vibration of the hydrogen atom. Due to the symmetrical nature of the group it is found that both of these bands are of only medium intensity. On the other hand the isopropenyl group gives rise to strong bands at about 1640 and 890 cm^{-1} .

The intensity of the isopropenyl band near 890 cm^{-1} is in fact so high that as little as 1 per cent. of a typical compound containing an isopropenyl group can be detected in a mixture using a cell thickness of only 0.025 mm . (Werner and Sutherland 1952).

The alcohol (Fig. 1) has a band of medium intensity at 828 cm^{-1} , using a cell of thickness 0.025 mm . This suggests the presence of an isopropylidene-type group $R_1R_2C=CH_2$, which is confirmed by the presence of a second band at 1674 cm^{-1} , also of medium intensity. The actual values found are close to those recorded by Barnard *et al.* (loc. cit.) for other terpenes containing isopropylidene groups.

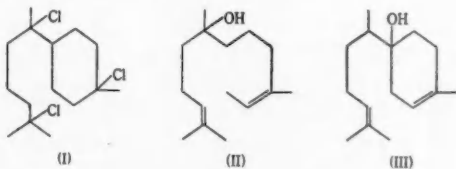
On the other hand, a careful examination of the spectrum in the region close to 890 cm^{-1} reveals only weak bands, although at the cell thickness used, an isopropenyl-type group $R_1R_2C=CH_2$ would have been expected to give a strong band. There is, in the 6μ -region, a band of medium intensity only at 1619 cm^{-1} , but this is lower than would be expected for an isopropenyl group (normally about 1645 cm^{-1}) and is in any case too weak. Similar cases in which overtone and combination bands occur in this region are cited by Barnard *et al.* (loc. cit.).

It should be noted that the infra-red spectra disposes of any possibility of conjugation of double bonds for such would have lowered the $C=C$ stretching frequencies to about 1600 cm^{-1} .

In proposing a formula for the alcohol we must therefore take into account the following points:

- (i) The facile conversion of the alcohol into bisabolene trihydrochloride (I).
- (ii) The optical activity of the alcohol in contrast to the inactivity of the bisabolene trihydrochloride.
- (iii) The nature of the unsaturation in the alcohol as indicated by infra-red spectra, which excludes conjugation and indicates two isopropylidene-type groups.

Only two formulae (II and III) will satisfy these conditions of which II



is the accepted formula for bisabolol.

II. EXPERIMENTAL

(a) *Distillation*.—The Anyme wood oil (250 ml.), on fractionation at 12 mm . through a 30 cm . Vigreux column, gave the fractions presented in Table 1.

Fractions 8–14 were mixed and used in the following experiments unless otherwise stated.

(b) *Preliminary Examination*.—(i) *Unsaturation*. Solutions of bromine tetrachloride and potassium permanganate in acetone were immediately decolorized.

(ii) *Test for Alcohols.* On treatment of the oil (1 ml.) with a small pellet of sodium only a slight evolution of hydrogen was obtained in the cold. Probably a secondary or tertiary alcohol. On treatment of the oil (1 ml.) with an equal volume of formic acid (100%) the oil was initially immiscible, but on warming a purple coloured homogeneous solution was formed, which soon separated into two layers—a reaction indicative of tertiary alcohols.

TABLE 1

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}	α_D^{20}
1	4	140–142	1.4934	–42
2	6	144–148	1.4940	–45
3	7	148–151	1.4944	–47
4	12	151–154	1.4964	–49
5	11	154–156	1.4964	–51
6	14	155–156	1.4975	–53
7	7	156–157	1.4977	–54
8	9	157	1.4977	–57
9	17	157	1.4976	–60
10	23	157	1.4976	–60
11	35	157	1.4976	–61
12	32	157	1.4976	–63
13	32	157	1.4976	–62
14	35	157	1.4976	–61
15	6	157	1.4976	—

(c) *Derivatives.*—(i) The alcohol did not react when heated with phthalic anhydride, either alone for 2 hr., or in benzene and pyridine respectively for 8 hr. No derivatives were formed on heating the alcohol with xenylcarbimide or on treatment with naphthylisocyanate, phenyl isocyanate, or benzoyl chloride under standard conditions.

(ii) *Dehydrogenation.* Treatment of the oil with either sulphur or platinum/carbon dehydrogenation catalyst gave products which failed to form picrate derivatives.

(iii) *Trihydrochloride Formation.* The oil (5 g.) was dissolved in anhydrous ether (5 ml.) and hydrogen chloride gas passed into the solution cooled to -15 – 20 °C. until the reaction mixture set to a solid red crystalline mass. The crystals were drained on a tile and recrystallized from ethyl acetate in the presence of carbon to give white crystalline flakes, m.p. 79.5 – 80 °C. Mixed m.p. with an authentic sample of bisabolene trihydrochloride showed no depression (Found: C, 57.55; H, 8.44; Cl, 33.72%. Calc. for $C_{15}H_{27}Cl_3$: C, 57.41; H, 8.61; Cl, 33.90%).

(iv) *Conversion of Trihydrochloride to Hydrocarbon.* The hydrochloride (15 g.) prepared as above was heated with anhydrous sodium acetate (45 g.) and glacial acetic acid (150 ml.) for 8 hr. on a steam-bath. The resultant oil was poured into water, extracted with ether, the extract washed with sodium carbonate solution, and finally with water. After drying over anhydrous sodium sulphate and removal of the solvent, the resultant oil (8 g., n_D^{20} 1.4875) was fractionated at 12 mm. to give the data of Table 2.

On treatment of fraction 1 (1 ml.) with hydrogen chloride, the trihydrochloride was reformed (m.p. 79 – 80 °C.) with the mixed m.p. unchanged.

(v) *Dehydration.* The oil (22 g.) was refluxed for 3 hr. in a Dean and Stark apparatus with benzene (100 ml.) containing concentrated sulphuric acid (0.5 ml.) until there was no further evolution of water (1.7 ml.). The benzene solution was washed first with sodium carbonate

solution and finally with water, dried over sodium sulphate, and the solvent removed. The residual oil (22 ml.) was fractionated at 12 mm. The results are presented in Table 3.

(vi) *Residue*. Fraction 3 formed the trihydrochloride with mixed m.p. undepressed.

(d) *Final Distillation and Examination*.—In the course of this investigation two efficient fractionation columns, namely the Lecky and Ewell (1940) type and the Bower and Cooke (1942) pattern, were acquired.

TABLE 2

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}	d_{15}^{15}
1	5	to 136	1.4915	0.8755
2	—	136–138	1.4915	0.8755
3	2	138	1.4860	—

Advantage was taken of their introduction to collect all the fractions and any remaining original Anyme wood oil, and to fractionate the mixture further through the Lecky and Ewell column, and finally through the Bower and Cooke column, in an endeavour to obtain increased purity of the alcohol fraction. The results of the final distillation are given in Table 4.

In view of the similarity in physical properties fractions 9–15 inclusive were mixed and used in the following examination, unless otherwise stated.

Molecular weight, determined by cryoscopic method, using benzene solvent (Found: 226, 219, 229. Calc. for $C_{15}H_{18}O$: 222). Combustion analysis (Found C, 80.94; H, 11.52%. Calc. for $C_{15}H_{18}O$: C, 81.02; H, 11.78%).

TABLE 3

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}
1	5.5	to 132	1.4962
2	8.5	132–134	1.4962
3	4.0	134–137	1.4962

(i) *Trihydromide*. The oil (5 ml.) was dissolved in anhydrous ether (5 ml.) and hydrogen bromide passed into the solution cooled to -20°C . A red solid crystalline mass formed after approximately half an hour. On repeated recrystallization from ethyl acetate and a little carbon, white crystalline flakes were obtained with constant melting point of 84°C . (corresponds to that recorded for bisabolene trihydrobromide).

(ii) *Dehydration with Formic Acid*. The oil (30 ml.) was refluxed for 3 hr. with formic acid (150 ml. of 98–100%). The reaction product was poured into water, extracted with ether, and washed with sodium carbonate solution and water. The dried ethereal extract yielded an oily residue which was distilled at 12 mm.

A mixture of 1.0 ml. each of fractions 1 and 4 (Table 5) gave the trihydrochloride, m.p. $79-80^{\circ}\text{C}$., undepressed on mixing with an authentic sample.

(iii) The oil (0.5 g.) was treated with excess *p*-phenylazophenylisocyanate in the presence of excess pyridine at 0 °C. for several hours and then at room temperature for 2 days.

TABLE 4

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{25}	α_D^{20}	d_4^{25}
1	4	to 125	1.4970	-36	0.0000
2	1	125	1.4985	-15	0.9703
3	4	150	1.5042	-33	0.9600
4	2	150-155	1.5013	-41	0.9888
5	7	155	1.5010	-44	0.9754
6	10	155	1.4975	-64	0.9537
7	11	155	1.4969	-66	0.9426
8	10	155	1.4970	-66.5	0.9404
9	10	155	1.4966	-67	0.9385
10	10	155	1.4970	-66.8	0.9376
11	10	155	1.4970	-67.1	0.9376
12	10	155	1.4972	-67.6	0.9377
13	10	155	1.4970	-67.6	0.9377
14	10	155	1.4970	-67.6	0.9376
15	10	155	1.4972	-67.6	0.9376

The reaction mixture was taken up in light petroleum, washed with water, filtered free of the insoluble urea, and then the aminoazobenzene removed by washing with dilute hydrochloric acid. The light petroleum solution was dried over anhydrous sodium sulphate and then allowed to evaporate leaving an orange-red oil which crystallized in the refrigerator.

TABLE 5

Fraction	Volume (ml.)	Boiling Range (°C.)	n_D^{20}
1	1	to 118	1.4976
2	5	118-122	1.4984
3	10	122-124	1.4951
4	7	124	1.5020

The orange-red oil was crystallized from light petroleum (b.p. 30-40 °C.) as orange crystals, m.p. 100-102 °C. Recrystallization from light petroleum (b.p. 60-80 °C.) yielded rosettes of orange needles of maximum m.p. 103-103.5 °C. Combustion analysis (Found: C, 74.8; H, 7.8%. Calc. for $C_{28}H_{28}O_3N_2$: C, 75.4; H, 7.92%).

(iv) *Hydrogenation of the Alcohol.* Approximately 0.2 g. of the alcohol was dissolved in 10 ml. of the solvent in the presence of 0.05 g. of Adam's catalyst and the whole shaken at room temperature and pressure until the absorption of hydrogen was complete (Found: 0.1810 g. in 10 ml. cyclohexane absorbed 54 ml. hydrogen at N.T.P. Calc. for $C_{15}H_{24}O$ containing two

double bonds 36.5 ml. hydrogen at N.T.P. Found: 0.2006 g. in 10 ml. acetic acid absorbed 68 ml. hydrogen at N.T.P. Calc. 61.8 ml. hydrogen at N.T.P.).

(v) *Hydrogenation of Hydrocarbon Regenerated from Trihydrochloride.* Approximately 0.2 g. of the hydrocarbon fraction 2 regenerated from the trihydrochloride was hydrogenated in 10 ml. of solvent, using cyclohexane in the first instance and glacial acetic acid in the second case, with 0.05 g. of Adam's catalyst (Found: 0.1511 g. hydrocarbon absorbed 47 ml. hydrogen at N.T.P. Calc. for $C_{18}H_{24}$ containing three double bonds 51.7 ml. hydrogen at N.T.P. Found: 0.2800 g. hydrocarbon absorbed 88 ml. hydrogen at N.T.P. Calc. 92.3 ml. hydrogen absorbed at N.T.P.).

(e) *Infra-red Spectrum Analysis.*—The infra-red spectrum of the alcohol was recorded using a Perkin-Elmer model 12C single beam instrument with sodium chloride optics. This instrument was calibrated against bands of water vapour in the 6μ -region and ammonia in the 10–12 μ -region (Oetjen, Kao, and Randall 1942). Comparison with the spectra used for the calibration indicated that the instrument resolved 6 cm^{-1} at 1700 cm^{-1} and 3 cm^{-1} at 1000 cm^{-1} . The material which was examined in demountable cells with rock-salt windows, was purified by vacuum distillation immediately prior to running the spectrum.

III. ACKNOWLEDGMENTS

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ALKALOIDS OF THE AUSTRALIAN RUTACEAE :
MEDICOSMA CUNNINGHAMII HOOK. F.

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Summary

The bark of *Medicosma cunninghamii* Hook. f. contains approximately 0.05 per cent. of an alkaloid $C_{17}H_{15}O_3N$ which has been named medicosmine and shown to be a 2,3-furoquinoline with a dimethylpyran ring fused in either the 5,6- or 6,7-positions (III or IV). It has been degraded to acetone, acetaldehyde, and a phenol which when methylated and oxidized gives 6-methoxy-4-hydroxy-1-methyl-2-quinolone, and 6- and 7-methoxy-4-hydroxy-1-methyl-2-quinolones have been synthesized for comparison. A dihydropyrano-4-methoxy-3-ethyl-2-quinolone is formed by hydrogenolysis of the furane ring. Further examples are reported of the preparation of isatins from 3-nitroso-2,4-dihydroxyquinolines.

I. INTRODUCTION

Medicosma cunninghamii Hook. f. is a small tree assigned by Engler and Prantl (1931) to the tribe Xanthoxyleae of the family Rutaceae and is the sole member of the genus. It occurs in the rain-forests of northern New South Wales and southern Queensland. The oil from the leaves has been examined by Sutherland (1949) who isolated from it 7-hydroxy-5-methoxy-8-acetyl-2,2-dimethylchromene (*alloeovodionol*) and 5,7-dimethoxy-6-acetyl-2,2-dimethylchromene (*evodionol methyl ether*). Webb (1949) records positive tests for alkaloids on an extract of the bark.

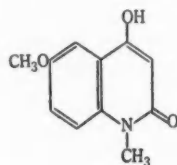
The bark contains approximately 0.05 per cent. of a weakly basic alkaloid, medicosmine, together with a trace of more strongly basic material. Medicosmine, $C_{17}H_{15}O_3N$, is optically inactive, contains one methoxyl but no methylimino-group, and on heating with methyl iodide is transformed to *isomedicosmine* containing one methylimino-, but no methoxyl group. Alcoholic hydrochloric acid demethylates the alkaloid to a phenol, normedicosmine, methylation of which yields *isomedicosmine*. Oxidation of medicosmine gives α -hydroxyisobutyric acid suggesting the presence of a 2,2-dimethylpyran ring. This is in agreement with the result of a Kuhn-Roth C-methyl determination, and is confirmed by the degradation of normedicosmine by 30 per cent. potassium hydroxide to acetone, acetaldehyde, and a phenol. The phenol was not isolated but was methylated directly to a product $C_{13}H_{11}O_3N$ containing one methoxyl and one methylimino-group. Oxidation of this substance with potassium permanganate and decarboxylation of the resulting acid gives 6-methoxy-4-hydroxy-1-methyl-2-quinolone (I). I and the 7-methoxy-isomer were

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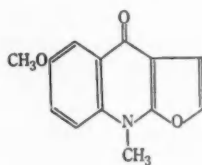
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synthesized for comparison by methylating the 6- and 7-methoxy-2,4-dihydroxyquinolines (Berinzaghi *et al.* 1945) and demethylating the 4-methoxyl group in the resulting 4,6 (or 7)-dimethoxy-1-methyl-2-quinolone with alcoholic hydrochloric acid.

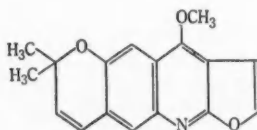
The formation of *isomedicosmine* and of *normedicosmine* is typical of the behaviour of the 4-methoxyfuroquinoline alkaloids, and the substance $C_{13}H_{11}O_3N$ formed by methylating the phenolic degradation product of *normedicosmine* is evidently a 1-methyl-6-methoxyfuroquinolone, the formation of which is analogous to that of *isokokusaginine* from *acronidine* (Lamberton and Price 1953). Assuming the linear tricyclic furoquinoline structure established for *dictamnine*, *acronycidine*, *kokusaginine*, and *acronidine*, the substance $C_{13}H_{11}O_3N$ will have structure II and there are two possible structures, III and IV, for *medicosmine*. The available evidence does not permit of differentiation between these two.



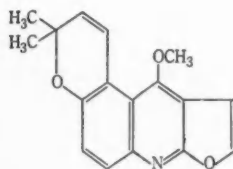
(I)



(II)



(III)

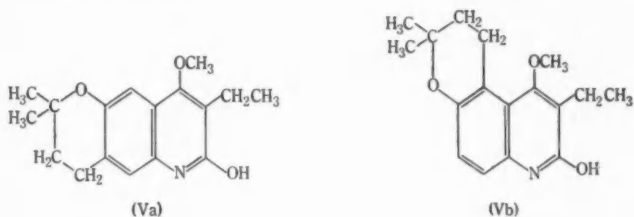


(IV)

In addition to the general resemblance of *medicosmine* to *acronidine* the position of attachment of the oxygen atom of the pyran ring to the benzenoid ring is the same in each. Consequently the formation, by hydrolytic breakdown of the dimethylpyran ring, of both acetone and acetaldehyde calls for no comment, having been discussed by Lamberton and Price for the case of *acronidine*. Another point of resemblance to *acronidine* is the competition between hydrogenation and hydrogenolysis which takes place when the alkaloid reacts with hydrogen in the presence of Raney nickel, resulting in a mixture of products, tetrahydromedicosmine and the 3-ethyl-2-quinolone (*Va* or *Vb*). *V* resembles the corresponding compound from *acronidine* being only soluble with difficulty in hot 1 per cent. hydrochloric acid and insoluble in alkali.* Accordingly, it

* In contrast to 3-alkyl-2-quinolones (personal communication from Dr. A. Langley Searles, see Lamberton and Price 1953) 2-methyl-3-ethyl-4-quinolone dissolves readily in hot 5 per cent. aqueous sodium hydroxide.

must be a 2-quinolone, from which it follows that the alkaloid is a 4-methoxy-2,3-furano-compound. The ease with which normedicosmine can be acetylated whereas V under the same conditions is recovered unchanged, confirms this linear tricyclic furoquinoline structure. Medicosmine is easily nitrated forming a mononitro-derivative in which the nitro-group is presumably located in the pyran ring, on the carbon atom adjacent to the benzenoid ring, cf. the bromination of acronycine (Brown *et al.* 1949). Normedicosmine couples in alkaline solution with diazonium salts but this does not differentiate between the alternative structures for the alkaloid.



Before employing direct methylation of the 2,4-dihydroxy-compound for the synthesis of I, the methylation of 2,4-dihydroxyquinoline with dimethyl sulphate and sodium hydroxide was examined. The product, 4-methoxy-1-methyl-2-quinolone, melts at 100 °C. instead of 68 °C. as reported by Friedländer and Müller (1887) who prepared it by the action of sodium methoxide on 4-chloro-1-methyl-2-quinolone. However, it forms a sesquihydrate melting at 68–69 °C. The melting points of 4-hydroxy-1-methyl-2-quinolone and its nitroso-derivative are higher than those recorded by Friedländer and Müller. The methylation of 6- and 7-methoxy-2,4-dihydroxyquinolines proceeded smoothly and gave better yields of the 4-methoxy-1-methyl-2-quinolones than could be obtained from 2,4-dihydroxyquinoline itself. The nitroso-derivatives of 7-methoxy-2,4-dihydroxyquinoline and of 7-methoxy-4-hydroxy-1-methyl-2-quinolone were converted to 6-methoxyisatin and 1-methyl-6-methoxyisatin respectively by treatment with acid as described by Lahey, Lamberton, and Price (1950). This would appear to be a convenient general method for the preparation of otherwise difficultly accessible isatins.

The ultraviolet absorption spectra of medicosmine and some derivatives will be presented in a later paper.

II. EXPERIMENTAL

All melting points are corrected except where otherwise stated. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Isolation of Medicosmine.*—Milled air-dried bark of *M. cunninghamii* (2.5 kg.) was extracted with methanol (Soxhlet), the extract evaporated, and the residue diluted with water. A trial experiment having established the absence of phenolic bases, the mixture was made alkaline with sodium carbonate, extracted with ether, and the ethereal solution shaken repeatedly with 10% hydrochloric acid until no further alkaloid was removed. The combined acid solutions were diluted with an equal volume of water, extracted with chloroform, and the chloroform extracts evaporated leaving a residue of crude *medicosmine*. Basification of the 5% aqueous

acid solution, extraction with chloroform, and evaporation gave a small amount of more strongly basic colourless material which melted at c. 240 °C. after crystallization from ethanol. The amount was too small for further investigation.

Crude medicosmine was extracted with benzene, the extract run through a column of alumina, and the eluted alkaloid crystallized from ethanol or from ethyl acetate-light petroleum as pale cream needles, m.p. 138.5–139.5 °C. Yield 1.25 g., 0.05%. Medicosmine dissolves readily in chloroform or ethyl acetate, less readily in alcohols, and is only sparingly soluble in water. A chloroform solution was optically inactive; alcoholic solutions showed a blue fluorescence (Found: C, 72.6; H, 5.5; N, 4.9; CH_3O , 11.2; $\text{CH}_3(\text{C})$, 2.5, 2.5%; CH_3N , nil.; mol. wt. (Rast), 278. Calc. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$: C, 72.6; H, 5.3; N, 5.0; CH_3O , 11.0 (one methoxyl); $\text{CH}_3(\text{C})$, 5.3% (one terminal methyl); mol. wt., 281).

Medicosmine is only sparingly soluble in 0.1N but dissolves readily in 1N hydrochloric acid, solution being followed by the separation of a hydrochloride. The base is extracted only slowly from a benzene solution by 1N hydrochloric acid.

Medicosmine picrate separated from ethanol as fine yellow needles, m.p. 190–191 °C. (Found: C, 54.3; H, 3.4; N, 10.9%. Calc. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N.C}_6\text{H}_5\text{O}_7\text{N}_3$: C, 54.1; H, 3.5; N, 11.0%).

Medicosmine picrolonate, yellow needles from ethanol, melted at 199–200 °C. (decomp., uncorr.) (Found: C, 59.4; H, 4.1; N, 12.6%. Calc. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N.C}_{10}\text{H}_8\text{O}_5\text{N}_4$: C, 59.4; H, 4.2; N, 12.8%).

Nitromedicosmine was prepared by dissolving the alkaloid (0.5 g.) in nitric acid (68%; 3 ml.), and, after 5 min., pouring into excess sodium bicarbonate solution. The mixture was extracted with chloroform and the residue, after evaporation of the solvent, dissolved in benzene and run through a column of alumina. The eluate contained 0.34 g. nitromedicosmine which separated from methanol as deep orange needles, m.p. 197–199 °C. (Found: C, 62.6; H, 4.2; N, 8.4%. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2$: C, 62.6; H, 4.3; N, 8.6%).

(b) *isoMedicosmine*.—Medicosmine (0.5 g.), heated in a sealed tube at 100 °C. for 4 hr. with methyl iodide (0.5 ml.), gave *isomedicosmine*, cream prisms from aqueous methanol, m.p. 226–227 °C. (Found: C, 72.6; H, 5.2; N, 5.1; CH_3N , 10.2%; CH_3O , nil. Calc. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}$: C, 72.6; H, 5.3; N, 5.0; CH_3N , 10.3%).

(c) *Oxidation of Medicosmine*.—Medicosmine was oxidized first with permanganate in acetone and then with alkaline permanganate according to the method described previously for acronidine (Lamberton and Price 1953). After removal of oxalic acid, the product was sublimed and crystallized from light petroleum giving α -hydroxyisobutyric acid, m.p. 78–79 °C. not depressed by admixture with an authentic specimen.

(d) *Normedicosmine*.—Hydrochloric acid (10N; 10 ml.) was added to a boiling solution of medicosmine (2 g.) in ethanol (70 ml.) and boiling continued for 10 hr. The sparingly soluble hydrochloride which separated was boiled with dilute aqueous sodium hydroxide (charcoal) and the filtered solution acidified with acetic acid to give *normedicosmine*, pale yellow prisms from toluene, m.p. 208–210 °C. Yield 1.3 g. When crystallized from aqueous methanol, the substance melted at c. 150 °C., resolidified, and finally melted again at 208–210 °C. It retains tenaciously half a molecule of water which could not be removed by drying at 100 °C. over phosphorus pentoxide in high vacuum (Found: C, 69.7; H, 5.0; N, 5.1%; CH_3O , nil. Calc. for $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N} \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 69.6; H, 5.1; N, 5.1%). When a solution of benzene diazonium chloride was added to a solution of normedicosmine in 10% sodium hydroxide, coupling occurred with precipitation of a reddish brown azo-compound. Methylation of normedicosmine with dimethyl sulphate and sodium hydroxide gave *isomedicosmine*, m.p. and mixed m.p. 226–227 °C. after crystallization from aqueous ethanol. *Acetyl normedicosmine*, obtained in good yield by heating normedicosmine with acetic anhydride and pyridine on the water-bath for half an hour, separated from aqueous ethanol as colourless flat needles, m.p. 184–185 °C. (Found: C, 69.9; H, 4.6%. Calc. for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$: C, 69.9; H, 4.9%).

(e) *Action of Alkali on Normedicosmine*.—Hydrolysis of normedicosmine by 30% aqueous potassium hydroxide was carried out under the conditions used for noracronidine (Lamberton and Price 1953), but the reaction was slower and was continued for 50 hr. A solution of the

combined 2,4-dinitrophenylhydrazones (0.41 g. from 0.65 g. normedicosmine) in benzene was chromatographed on alumina taking five fractions. Each was evaporated to dryness and the residues crystallized from ethanol with the following results:

Fraction	Amount (mg.)	M.p. (°C.)
1	35	120–122
2	80	c. 106
3	75	105–120
4	100	118–130
5	110	140–150

Fractions 4 and 5 were combined, and repeatedly crystallized from benzene, and finally from ethanol, to give acetaldehyde-2,4-dinitrophenylhydrazone, m.p. 166–168 °C. either alone or mixed with an authentic specimen (Found: C, 42.9; H, 3.6%. Calc. for $C_8H_9O_4N_4$: C, 42.9; H, 3.6%).

Fractions 2 and 3 and the mother liquors from 1 and 4 were combined and rechromatographed taking six fractions. The first two, melting at 123–126 and 119–122 °C. respectively, were combined with fraction 1 and crystallized from ethanol giving acetone-2,4-dinitrophenylhydrazone, m.p. 125–126.5 °C. either alone or mixed with an authentic specimen (Found: C, 45.5; H, 4.3%. Calc. for $C_9H_{10}O_4N_4$: C, 45.4; H, 4.2%). The proportion of each 2,4-dinitrophenylhydrazone in the mixture was not determined but it was estimated that acetone-2,4-dinitrophenylhydrazone constituted 30–50%.

The alkaline reaction mixture after distillation of the volatile products was diluted with an equal volume of water and shaken with dimethyl sulphate (5 ml. in three portions). Extraction with chloroform gave a brownish crystalline solid (0.38 g.) which was boiled with water (charcoal), the aqueous solution cooled and filtered, giving colourless needles (0.19 g.). After recrystallization from benzene the substance melted at 213.5–215.5 °C. (Found: C, 68.3; H, 4.9; O, 20.8; N, 5.8; CH_3O , 13.4; CH_3N , 14.7%. Calc. for $C_{13}H_{11}O_3N$: C, 68.1; H, 4.8; O, 21.0; N, 6.1; CH_3O , 13.4 (one methoxyl); CH_3N , 12.7%).

(f) *Oxidation of the Degradation Product $C_{13}H_{11}O_3N$* .—A solution of the substance $C_{13}H_{11}O_3N$ (0.4 g.) in acetone (70 ml.) was oxidized at room temperature by potassium permanganate (0.8 g.), the manganese dioxide precipitate extracted with dilute aqueous sodium hydroxide, and the extract acidified with acetic acid. The yellow precipitate suspended in hydrochloric acid (5N; 20 ml.) was boiled under reflux for several hours until all had dissolved. The solid which crystallized on cooling was dissolved in dilute aqueous sodium hydroxide (charcoal) and the filtered solution acidified with acetic acid. The resulting precipitate crystallized from ethanol as colourless prisms, m.p. 278–279 °C. (uncorr.) either alone or mixed with a synthetic specimen of 6-methoxy-4-hydroxy-1-methyl-2-quinolone (Found: C, 64.4; H, 5.4; N, 6.6; CH_3O , 15.9; CH_3N , 14.5%. Calc. for $C_{11}H_{11}O_3N$: C, 64.4; H, 5.4; N, 6.8; CH_3O , 15.1 (one methoxyl) CH_3N , 14.1%).

A portion of quinolone from the alkaloid was dissolved in dilute aqueous sodium hydroxide, sodium nitrite (1.1 mole) added, and the solution acidified with dilute sulphuric acid. The resulting precipitate crystallized from ethanol as red needles which melted with decomposition at 211–212 °C. after darkening from 200 °C. A mixture with 6-methoxy-4-hydroxy-3-nitroso-1-methyl-2-quinolone, and that compound itself, showed the same melting point behaviour (Found: N, 11.7; CH_3O , 13.7%. Calc. for $C_{11}H_{10}O_4N_2$: N, 12.0; CH_3O , 13.2%).

(g) *Hydrogenation of Medicosmine*.—Medicosmine (0.5 g.) in ethanol (250 ml.), hydrogenated over Raney nickel, absorbed 117 ml. hydrogen at 24 °C. and 761 mm.; calc. for three moles, 130 ml. The solution was filtered, evaporated, and the residue (0.41 g.) dissolved in benzene and chromatographed on alumina giving two products. The first, tetrahydromedicosmine (0.26 g.) was eluted by benzene and crystallized from methanol as colourless needles, m.p. 200–201 °C.

(Found: C, 71.8; H, 6.9; $\text{CH}_3(\text{C})$, 4.5, 4.4%. Calc. for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$: C, 71.6; H, 6.7; $\text{CH}_3(\text{C})$, 5.3% (one $\text{CH}_3(\text{C})$ group)). Tetrahydromedicosamine is insoluble in hot 4% aqueous sodium hydroxide and gives no colour with ferric chloride. It dissolves easily in cold 1% hydrochloric acid. It was recovered unchanged (m.p. and mixed m.p.) after attempted hydrogenation over Raney nickel in ethanol.

The second product, Va or Vb (0.13 g.), was eluted by chloroform and crystallized from methanol as colourless prisms, m.p. 259–261 °C. (uncorr.) (Found: C, 71.1; H, 7.4; CH_3O , 10.9; $\text{CH}_3(\text{C})$, 8.9, 9.4%. Calc. for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$: C, 71.1; H, 7.3; CH_3O , 10.8; $\text{CH}_3(\text{C})$, 5.2% (one $\text{CH}_3(\text{C})$ group)). This compound is insoluble in hot 4% aqueous sodium hydroxide, gives no colour with ferric chloride and is only sparingly soluble in boiling 1% hydrochloric acid. It was recovered unchanged (m.p. and mixed m.p.) after heating on the water-bath with acetic anhydride and a little pyridine for half an hour.

2-Methyl-3-ethyl-4-hydroxyquinoline was found to be readily soluble in hot 5% aqueous sodium hydroxide. It was prepared as described by Conrad and Limpach (1891) and melted at 296–297 °C. Conrad and Limpach report m.p. 290 °C.; Gillis, Lions, and Ritchie (1939) report m.p. 275 °C. for a specimen prepared by ethylating ethyl β -anilinoacrylate.

(h) *Methylation of 2,4-Dihydroxyquinoline*.—A solution of 2,4-dihydroxyquinoline (5.5 g.) in aqueous sodium hydroxide (10%; 20 ml.) was shaken with four 27-ml. portions of dimethyl sulphate, sodium hydroxide (20%; 140 ml.) being added with each portion of dimethyl sulphate. The reaction mixture was shaken with chloroform, the chloroform evaporated, and the residue (1.43 g.) exhaustively extracted with light petroleum (b.p. 40–60 °C.). The combined light petroleum extracts were concentrated, allowed to crystallize, and the product dissolved in benzene and chromatographed on alumina. 4-Methoxy-1-methyl-2-quinolone (0.73 g.), eluted by benzene, crystallized from light petroleum as colourless needles, m.p. 65–66 °C. (air-dried), 99.5–100 °C. after drying in a vacuum at 60 °C. (Found: C, 69.9; H, 5.8; CH_3O , 16.2; CH_3N , 10.4%. Calc. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$: C, 69.8; H, 5.8; CH_3O , 16.4%; CH_3N , 15.3%). The substance separated from aqueous methanol as a sesquihydrate, m.p. 68–69 °C. (Found (on an air-dried specimen): loss on drying, 12.5%. Calc. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N} \cdot 1\frac{1}{2}\text{H}_2\text{O}$: 12.5%). Boiling for 1½ hr. with 5N hydrochloric acid gave the hydrochloride of 4-hydroxy-1-methyl-2-quinolone which was dissolved in sodium hydroxide and the phenol precipitated by acidification with acetic acid. It separated from ethanol as colourless prisms, m.p. 274.5–275.5 °C. (uncorr.); Friedländer and Müller (1887) record m.p. 259–260 °C. (Found: C, 68.9; H, 5.2; N, 7.8%; CH_3O , nil. Calc. for $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$: C, 68.6; H, 5.1; N, 8.0%). 3-Nitroso-4-hydroxy-1-methyl-2-quinolone, prepared as described under (f), separated from ethanol as orange needles which darkened at 215 °C. and decomposed at 220 °C.; it is described by Friedländer and Müller as red needles decomposing at 188 °C. (Found: C, 58.6; N, 4.1; N, 13.6%. Calc. for $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2$: C, 58.8; H, 3.9; N, 13.7%).

(i) *Syntheses of 6- and 7-Methoxy-4-hydroxy-1-methyl-2-quinolones*.—(i) 6-Methoxy-2,4-dihydroxyquinoline, prepared according to the method of Berinzaghi *et al.* (1945) but employing the magnesium ethoxy derivative of malonic ester, melted at 322 °C. (decomp., uncorr.). Methylation with dimethyl sulphate and sodium hydroxide (20%) gave 4,6-dimethoxy-1-methyl-2-quinolone, which was purified by passing a chloroform solution through alumina and crystallized from benzene-light petroleum. It formed colourless needles, m.p. 145–146 °C. (Found: N, 6.5; CH_3O , 27.9%. Calc. for $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}$: N, 6.4; CH_3O , 28.3% (two methoxyls)). Boiling with 5N hydrochloric acid for 1 hr. and cooling gave the hydrochloride of 6-methoxy-4-hydroxy-1-methyl-2-quinolone from which the phenol was recovered by acidification of an aqueous alkaline solution with acetic acid. The compound crystallized from ethanol as colourless prisms, m.p. 278–279 °C. (uncorr.) (Found: C, 64.8; H, 5.3; N, 6.5; CH_3O , 15.4; CH_3N , 14.1%. Calc. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$: C, 64.4; H, 5.4; N, 6.8; CH_3O , 15.1; CH_3N , 14.1%). 6-Methoxy-4-hydroxy-3-nitroso-1-methyl-2-quinolone, prepared as described under (f) crystallized from

* Although 4-methoxy-1-methyl-2-quinolone is readily hydrolysed by 5N hydrochloric acid, the rate of hydrolysis with hydriodic acid in the methoxyl determination is very low. The maximum value of 16.2% methoxyl was obtained after 1½ hr. heating. After 1 hr. the result was 12.0%.

ethanol as red needles which darkened at 200 °C. and melted with decomposition at 211–212 °C. (Found: N, 11.8%. Calc. for $C_{11}H_{18}O_4N_2$: N, 12.0%).

(ii) *4,7-Dimethoxy-1-methyl-2-quinolone*, prepared by methylating 7-methoxy-2,4-dihydroxy-quinoline as described for the 6-methoxy-isomer, crystallized from benzene-light petroleum as colourless needles, m.p. 142.5–143.5 °C. (Found: N, 6.4; CH_3O , 28.0%. Calc. for $C_{11}H_{18}O_4N$: N, 6.4; CH_3O , 28.3% (two methoxys)). Demethylation by 5N hydrochloric acid gave: *7-methoxy-4-hydroxy-1-methyl-2-quinolone*, colourless needles from ethanol 292–293 °C. (decomp., uncorr.) (Found: N, 7.0; CH_3O , 15.1%. Calc. for $C_{11}H_{18}O_3N$: N, 6.8; CH_3O , 15.1%).

7-Methoxy-4-hydroxy-3-nitroso-1-methyl-2-quinolone crystallized from ethanol as long yellow needles, m.p. 185–187 °C. (Found: N, 11.9; CH_3O , 13.4%. Calc. for $C_{11}H_{18}O_4N_2$: N, 12.0; CH_3O , 13.2%).

(j) *6-Methoxyisatin* and *1-Methyl-6-methoxyisatin*.—(i) 7-Methoxy-3-nitroso-2,4-dihydroxy-quinoline (0.5 g.), refluxed with aqueous sulphuric acid (30%) for 2 hr., dissolved slowly with frothing. The solution was cooled, diluted with water, and repeatedly extracted with chloroform giving 6-methoxyisatin (0.2 g.), orange plates from ethanol, m.p. 235–236 °C. Salzer, Timmler, and Andersag (1948) record m.p. 230 °C., presumably uncorrected (Found: N, 8.0; CH_3O , 17.4%. Calc. for $C_9H_8O_3N$: N, 7.9; CH_3O , 17.5%). It dissolved in aqueous alkali giving a red solution which faded rapidly to yellow.

(ii) *1-Methyl-6-methoxyisatin*, prepared in the same manner from 7-methoxy-4-hydroxy-3-nitroso-1-methyl-2-quinolone, separated from ethanol as reddish orange needles, m.p. 195–197 °C. (Found: N, 7.3; CH_3O , 16.6%. Calc. for $C_{10}H_8O_3N$: N, 7.3; CH_3O , 16.2%).

III. ACKNOWLEDGMENTS

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THE ALKALOIDS OF *GYROCARPUS AMERICANUS* JACQ.

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Summary

The bark of *Gyrocarpus americanus* Jacq. contains 0.4–0.6 per cent. phaeanthine and 0.6–0.7 per cent. of the quaternary base *d*-magnocurarine. The leaves contain 0.03 per cent. phaeanthine only.

I. INTRODUCTION

Gyrocarpus americanus Jacq., a deciduous tree of moderate size belonging to the family Hernandiaceae, is a variable species distributed throughout the tropics. Webb (1952) records strong positive tests for alkaloids with an extract of the bark. The bark of the tree contains two alkaloids, a ditertiary base $C_{38}H_{42}O_6N_2$ (0.4–0.6 per cent.), and a water-soluble quaternary base $C_{19}H_{24}O_3N^+$ (0.6–0.7 per cent.). The former has been identified as phaeanthine by comparison of the base, its picrate, aurichloride, and methiodide with authentic specimens, and in view of the statement of Bick and Todd (1948) that mixed melting points in the bisbenzylisoquinoline series are not wholly satisfactory as a means of establishing identity, these data (see Table 1) have been supplemented by X-ray powder photographs and by R_F values with butanol-5 per cent. acetic acid. In addition, the alkaloid was converted to the previously reported methine base of melting point 173 °C. and was oxidized to 2-methoxydiphenyl ether 5,4'-dicarboxylic acid. Phaeanthine, originally isolated from *Phaeanthus ebracteolatus* (Presl.) Merrill and recognized as a bisbenzylisoquinoline by Santos (1931, 1932a), was assigned one of two alternative structures by Kondo and Keimatsu (1935), who showed it to be an optical antipode of tetrandrine. Recent work by Tomita and his collaborators (Fujita and Murai 1951; Tomita, Fujita, and Murai 1951) distinguishes between the alternative structures and shows that phaeanthine is I, both asymmetric centres being laevorotatory. We find the melting point of phaeanthine to be 12–14 °C. higher than reported previously.

The quaternary base $C_{19}H_{24}O_3N^+$, isolated by means of its sparingly soluble picrate, is dextrorotatory ($[\alpha]_D +106^\circ$) and contains one methoxyl group and two methyl groups attached to nitrogen. It is converted by methylation to a quaternary iodide containing three methoxyl groups and two methyl groups attached to nitrogen and thus is isomeric with the alkaloid magnocurarine (II; $[\alpha]_D -91^\circ$) recently described by Tomita, Inubushi, and Yamagata (1951). However, a specimen of *OO*-dimethylmagnocurarine iodide (*OO**N*-trimethylcoclaurine methiodide), kindly supplied by Professor Tomita, depressed the melting point of the methylated iodide of the *G. americanus* base. On the

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other hand, the optically inactive methine, $C_{21}H_{27}O_3N$, formed by Hofmann degradation of the methylated iodide, is identical with the methine obtained from dimethylmagnocurarine. Ethylation of the *G. americanus* base gives the

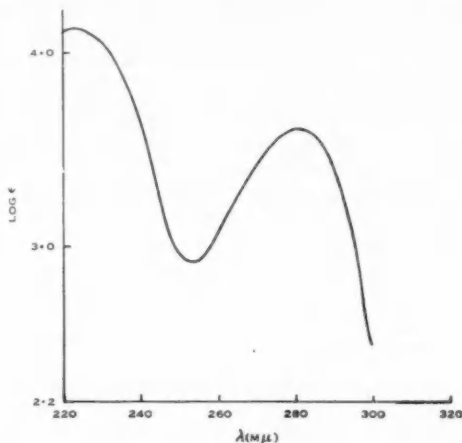


Fig. 1.—Ultraviolet absorption spectrum of *d*-magnocurarine in water.

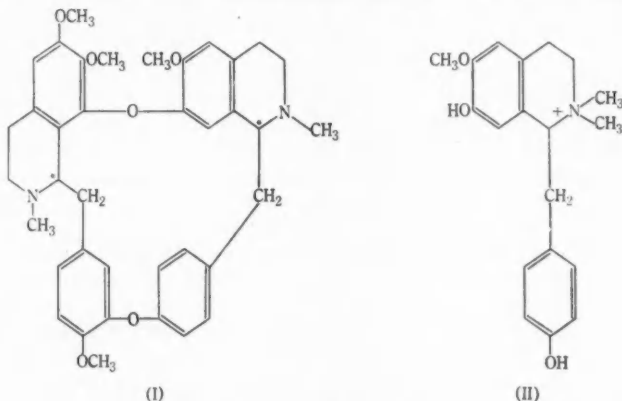
TABLE I
COMPARISON OF THE PROPERTIES OF PHAEANTHINE FROM *G. AMERICANUS* AND FROM
P. EBRACTEOLATUS

Derivative	Phaeanthine from <i>P. ebracteolatus</i>		Phaeanthine from <i>G. americanus</i>
	Santos (1931)	Present Work	
Base ..	M.p. 210 °C. [α] _D ³⁰ -278°	M.p. 220-222 °C. (corr.) [α] _D ²⁵ -272°	M.p. 222-224 °C. (corr.) [α] _D ¹⁷ -284°
Picrate ..	M.p. 263 °C. (decomp., vacuum)	M.p. 257-258 °C. (corr., decomp.)	M.p. 257-258 °C. (corr., decomp.)
Aurichloride	M.p. 170-171 °C. (decomp., vacuum)	M.p. 171 °C. (corr., decomp.)	M.p. 171 °C. (corr., decomp.)
Methiodide ..	M.p. 265 °C. (decomp., vacuum)	M.p. 264.5-265.5 °C. (corr., decomp.)	M.p. 267-268 °C. (corr., decomp.)

OO-diethyl iodide, $C_{23}H_{33}O_3NI \cdot H_2O$, from which was obtained by Hofmann degradation an *OO*-diethylmethine melting at the same temperature as the corresponding derivative of magnocurarine. Oxidation of this methine gave

p-ethoxybenzoic acid and, after a second Hofmann degradation followed by hydrogenation, 3-ethoxy-4-methoxy-6-ethylbenzoic acid. It follows that the *G. americanus* base is *d*-magnocurarine. The ultraviolet absorption spectrum (Fig. 1) shows two maxima: λ_{\max} . 282 $m\mu$, $\log \epsilon_{\max}$. 3.62 and λ_{\max} . 225 $m\mu$, $\log \epsilon_{\max}$. 4.12, and differs in one respect from that of *l*-magnocurarine reported by Tomita, Inubushi, and Yamagata (1951). In the absorption curve published by these authors the band at $\sim 280 m\mu$ has an intensity ($\log \epsilon_{\max}$. ~ 4.2) several times too great for a benzyltetrahydroisoquinoline.*

The leaves of *G. americanus* contain 0.03 per cent. phaeanthine but no water-soluble alkaloid. *d*-Magnocurarine, like the *l*-base, exhibits curariform activity; the results of pharmacological examination will be published elsewhere.



II. EXPERIMENTAL

All melting points are corrected except where otherwise stated. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) *Isolation of the Alkaloids.*—(i) Milled air-dried bark (25 kg.), collected in the Rockhampton district of Queensland, was exhaustively extracted with ethanol at 45–50 °C., the extract evaporated to a small volume, and the residue stirred three times with 1.3% sulphuric acid. The combined acid solutions (c. 70 l.) were washed with trichloroethylene, basified with sodium carbonate, and the tertiary base extracted with trichloroethylene. The aqueous alkaline liquors were neutralized, evaporated under reduced pressure to c. 20 l., and saturated methanolic picric acid solution added until no further precipitation of picrate took place. Crystallization from aqueous ethanol gave brownish yellow crystals of the quaternary picrate. Yield 265 g. equivalent to 0.6% base. The trichloroethylene solution of crude tertiary base was evaporated, the residue extracted with 2% hydrochloric acid, and the acid solution basified with sodium carbonate and extracted three times with ether and, finally, three times with chloroform. Evaporation of the ether extracts gave solid alkaloid but the chloroform extracts after removal of solvent consisted of an intractable gum which necessitated retreatment with 2% hydrochloric

* Professor Tomita (personal communication) has confirmed that the published value ($\log \epsilon_{\max}$. ~ 4.2) for the intensity of this band in the spectrum of *l*-magnocurarine is incorrect and should be 3.61. We are indebted to Dr. E. Gellert for drawing our attention to the discrepancy.

acid. The acid extracts were basified with sodium carbonate and the alkaloid again shaken out, first with ether and then with chloroform. Repetition of acid treatment of the chloroform extracts gave a little more alkaloid extracted by ether and a small quantity of gummy phenolic base which was not further investigated. Crystallization of the ether-extracted base from acetone gave 108.6 g., 0.43%. The yields of both tertiary and quaternary bases were higher in small-scale extractions, the former up to 0.6%.

(ii) Milled air-dried leaves (780 g.) were extracted with methanol (Soxhlet), the solvent evaporated, and the residue extracted four times with hot 2% hydrochloric acid. The alkaloid, recovered after basification with sodium carbonate and extraction with chloroform, was dissolved in benzene and chromatographed on alumina giving phaeanthine (0.22 g., 0.03%). No quaternary picrate was precipitated on addition of picric acid to the neutralized aqueous liquors.

(iii) *P. ebracteolatus* bark, extracted by ethanolic hydrochloric acid, gave phaeanthine which crystallized from methanol as colourless needles, m.p. 220–222°C., $[\alpha]_D^{25} -272^\circ$ (c, 3.99 in chloroform). Yield 0.3%. The aqueous liquors were not examined.

(b) *Phaeanthine*.—(i) Recrystallization of the tertiary base from *G. americanus* bark from acetone or methanol gave colourless needles, m.p. 222–224°C.* undepressed by admixture with authentic phaeanthine, $[\alpha]_D^{17} -284^\circ$ (c, 4.015 in chloroform) (Found: C, 73.2; H, 6.9; N, 4.8; O, 15.4; CH_3O , 19.6; CH_3N , 8.7%; mol. wt. (cryoscopic in benzene), 617,620. Calc. for $\text{C}_{28}\text{H}_{48}\text{O}_6\text{N}_2$: C, 73.3; H, 6.8; N, 4.5; O, 15.4; CH_3O , 19.9 (four methoxyls); CH_3N , 9.3% (two methylimino-groups); mol. wt., 622). R_F values with butanol-5% acetic acid were: authentic phaeanthine, 0.33; phaeanthine from *G. americanus*, 0.31. The Debye-Scherrer diagrams of authentic phaeanthine and of the alkaloid from *G. americanus* were identical. The picrate melted at 257–258°C. (decomp.) and a mixture with an authentic specimen (m.p. 257–258°C., decomp.) showed the same behaviour (Found: C, 55.4; H, 4.7; N, 10.5%. Calc. for $\text{C}_{28}\text{H}_{48}\text{O}_6\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$: C, 55.6; H, 4.4; N, 10.4). The dimethide melted at 267–268°C. (decomp.) and a mixture with an authentic specimen (m.p. 264.5–265.5°C. decomp.) at 265.5–266.5°C. (decomp.) (Found: C, 49.0; H, 5.9; I, 26.2; CH_3O , 12.7%. Calc. for $\text{C}_{48}\text{H}_{80}\text{O}_8\text{N}_4 \cdot 4\text{H}_2\text{O}$: C, 49.1; H, 5.7; I, 26.0; CH_3O , 12.7%). The aurichloride melted at 171°C. (decomp.) alone or mixed with authentic phaeanthine aurichloride.

Permanganate oxidation of the alkaloid as described by Santos (1932b) gave 2-methoxydiphenyl ether 5,4'-dicarboxylic acid, m.p. 306.5–307.5°C. (uncorr.) (Found: C, 62.1; H, 4.5; CH_3O , 10.7%. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}_4$: C, 62.5; H, 4.2; CH_3O , 10.8%). The dimethyl ester of the acid melted at 96–97°C. (Found: C, 64.7; H, 5.4%. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_6$: C, 64.6; H, 5.1%).

Hofmann degradation of the alkaloid dimethohydroxide gave a methine base, m.p. 173.5–174.5°C. (Found: C, 73.7; H, 6.9; N, 4.5%. Calc. for $\text{C}_{26}\text{H}_{46}\text{O}_4\text{N}_2$: C, 73.8; H, 7.1; N, 4.3%).

(ii) The tertiary base from the leaves of *G. americanus* was identified as phaeanthine by m.p. and mixed m.p. of the base and its picrate. It had R_F value 0.33 with butanol-5% acetic acid.

(c) *d-Magnocurarine*.—(i) The quaternary picrate crystallized from aqueous acetone as long yellow needles, m.p. 181.5–183°C. Tomita, Inubushi, and Yamagata (1951) record m.p. 169–172°C. for *l*-magnocurarine picrate and we find that unless thoroughly dried *d*-magnocurarine picrate has a lower m.p. due to retention of solvent (Found (after drying in a vacuum at 100°C.): C, 55.6; H, 5.2; N, 10.1; CH_3O , 6.8, 6.8; CH_3N , 7.9%. Calc. for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{N}^+ \cdot \text{C}_6\text{H}_5\text{O}_7\text{N}_3^-$: C, 55.4; H, 4.8; N, 10.3; CH_3O , 5.7 (one methoxyl); CH_3N , 10.7% (two methyl groups attached to nitrogen)).

* Specimens of phaeanthine isolated in preliminary small-scale experiments, crystallized from aqueous methanol, and melting at 208–210°C. gave perfectly satisfactory analytical values. Low melting (208–210°C.) material was considerably more soluble in methanol than higher melting (220°C.) and it was only when sufficient alkaloid became available to crystallize from anhydrous methanol that the higher melting point was attained.

To a solution of the picrate (5 g.) in boiling ethanol (100 ml.), hydrochloric acid (10%; 100 ml.) was added gradually, the mixture cooled, and shaken several times with chloroform. The chloroform extracts were washed with 10% hydrochloric acid and the aqueous acid solutions again shaken with chloroform and evaporated to dryness under reduced pressure. The resulting pale brown resinous hydrochloride was readily soluble in water or methanol; its solutions gave a bluish green Fe^{+++} reaction.

d-Magnocurarine was liberated from a methanolic solution of the hydrochloride by the addition of methanolic potassium hydroxide (1 mole) and the phenol-betaine crystallized from aqueous methanol as colourless prisms, m.p. 198–199 °C. (decomp.), $[\alpha]_D^{22} + 106^\circ$ (c, 0.98 in water) (Found (after drying in a vacuum at 100 °C.): C, 69.2; H, 7.7; N, 4.1; CH_3O , 11.9, 14.1, 12.8; CH_2N , 16.3, 14.9%. Calc. for $\text{C}_{19}\text{H}_{28}\text{O}_4\text{N}$: C, 68.9; H, 7.6; N, 4.2; CH_3O , 9.4; CH_2N , 17.5% (two methyl groups attached to nitrogen)).

The high and variable methoxyl values demand some comment. Tomita, Inubushi, and Yamagata obtained similar results and attributed them to the elimination of some methyl iodide from the *N*-methyl groups. *d*-Magnocurarine picrate (see above) also gives high methoxyl values but, surprisingly, this abnormality was not encountered with *OO*-dimethylmagnocurarine iodide. Analytical data for tubocurarine chloride and *OO*-dimethyltubocurarine iodide reported by both King (1935) and Dutcher (1946) show the same phenomenon, namely, high methoxyl values for the phenolic alkaloid but not for the methyl ether. While Tomita's explanation is probably correct, the possibility that the high methoxyl values may be partly due to contamination by methylated derivatives should not be overlooked. However, paper chromatograms of the following samples run with butanol-5% acetic acid each showed one spot only, at R_F 0.42: (1) The alkaloid hydrochloride prepared from the picrate. (2) The phenol-betaine as precipitated from a solution of the hydrochloride. (3) The phenol-betaine three times recrystallized from aqueous methanol (50% recovery). (4) Phenol-betaine recovered from mother liquors after the recrystallization of (3) (10% of original material).

(ii) A solution of the hydrochloride (from 10 g. picrate) in aqueous potash (10%; 50 ml.) was shaken with dimethyl sulphate (16.2 ml.) in small portions, the reaction mixture allowed to stand for 2 hr., warmed on the water-bath, and neutralized with sodium carbonate. Extraction with chloroform and crystallization from ethyl acetate gave *OO*-dimethylmagnocurarine methosulphate in good yield as colourless rosettes of needles, m.p. 158–158.5 °C. Finkelstein (1951) reports m.p. 174–175 °C. for the *dl*-compound, and Kondo and Kondo (1930) report m.p. 175 °C. for both synthetic (*dl*-) and for a specimen prepared from *l*-coclaurine* (Found: C, 58.4; H, 6.8; N, 2.9; S, 7.1; CH_3O , 26.9%. Calc. for $\text{C}_{21}\text{H}_{28}\text{O}_5\text{N}^+\cdot\text{CH}_3\text{SO}_3^-$: C, 58.3; H, 6.8; N, 3.1; S, 7.1; CH_3O , 27.4% (four methoxyls)).

Methylation of *d*-magnocurarine with methyl iodide and sodium methoxide in methanol gave *OO*-dimethyl-*d*-magnocurarine iodide, straw coloured needles from water, m.p. 115 °C. (decomp.), or after drying at 100 °C., 139 °C. (decomp.). An authentic sample of *OO*-dimethyl-*l*-magnocurarine iodide, after drying at 100 °C., melted at the higher temperature but a mixed m.p. with the iodide from the *G. americanus* base was depressed 10–15 °C. R_F values with butanol-5% acetic acid were 0.52 for both iodides (Found (on material dried at 100 °C.): C, 51.6; H, 6.1; N, 2.7; CH_3O , 18.6, 18.7, 18.5; CH_2N , 10.2%. Calc. for $\text{C}_{21}\text{H}_{28}\text{O}_5\text{N}\cdot\text{H}_2\text{O}$: C, 51.7; H, 6.2; N, 2.9; CH_3O , 19.1 (three methoxyls); CH_2N , 11.9% (two methyl groups attached to nitrogen), $[\alpha]_D^{22} + 190^\circ$ (c, 0.99 in methanol)).

Hofmann degradation of the methylated quaternary base gave the methine base, colourless needles, m.p. 85.5–86.5 °C. undepressed by admixture with the methine base from *l*-magnocurarine. R_F values for butanol-5% acetic acid were 0.49 for both specimens (Found: C, 74.2; H, 8.0; N, 4.3%. Calc. for $\text{C}_{21}\text{H}_{21}\text{O}_5\text{N}$: C, 73.9; H, 7.9; N, 4.1%). A solution in chloroform was optically inactive.

(iii) Ethylation of *d*-magnocurarine (from 13.4 g. picrate) with ethyl iodide and methanolic potassium hydroxide gave *OO*-diethyl-*d*-magnocurarine iodide, colourless needles from water,

* Tomita and Kusuda (1952) have recently shown that natural coclaurine from *Cocculus laurifolius* is the *dl*- and not the *l*-form as supposed by Kondo and Kondo.

m.p. 72.5–73.5 °C. Yield 7.6 g.* On drying at 60 °C. in a vacuum the m.p. rose to 93–94 °C. but dropped rapidly to 72.5–73.5 °C. in air (Found (on material melting at 72.5–73.5 °C.): C, 53.6; H, 6.6; N, 2.7%. Calc. for $C_{22}H_{22}O_2NIH_2O$: C, 53.6; H, 6.6; N, 2.7%). The R_F value with butanol-5% acetic acid was 0.62. Hofmann degradation of *OO*-diethyl-*d*-magnocurarine gave the methine, m.p. 77.5–78 °C. (Found: C, 74.6; H, 8.4; N, 4.0%. Calc. for $C_{22}H_{21}O_2N$: C, 74.8; H, 8.4; N, 3.8%). Oxidation of the methine gave *p*-ethoxybenzoic acid, m.p. and mixed m.p. with an authentic specimen, 195–196 °C. (Found: C, 65.2; H, 6.2%. Calc. for $C_9H_{10}O_3$: C, 65.1; H, 6.0%). The second oxidation product was recovered by evaporating the aqueous solution to dryness under reduced pressure and extracting with ethanol. The ethanol extract was evaporated to dryness, the residue dissolved in water and the solution basified, shaken with chloroform, and then methylated and degraded as described by Tomita, Inubushi, and Yamagata (1951) giving 3-ethoxy-4-methoxy-6-ethylbenzoic acid, m.p. and mixed m.p. with an authentic specimen, 139.5–140 °C. (Found: C, 64.4; H, 7.0%. Calc. for $C_{13}H_{16}O_4$: C, 64.3; H, 7.1%).

(iv) The ultraviolet absorption spectrum was measured in aqueous solution by means of a Beckmann model DU spectrophotometer.

III. ACKNOWLEDGMENTS

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* Tomita, Inubushi, and Yamagata (1951) did not crystallize *OO*-diethyl-*d*-magnocurarine iodide.

SHORT COMMUNICATIONS

A.C. POLAROGRAPHIC-TENSAMMETRIC TRANSITION WAVES*

By B. BREYER† and S. HACOBIAN†

It has been shown in previous communications that wave shaped current-voltage curves are obtained when a small sinusoidal alternating potential is superimposed onto the direct potential applied to a dropping mercury electrode in the presence of either dischargeable ions (A.C. polarography; cf. Breyer, Gutmann, and Hacobian 1950*a*, 1950*b*, 1951; Breyer and Hacobian 1951*a*, 1951*b*) or of surface active substances (Tensammetry; Breyer and Hacobian 1952). In the case of A.C. polarography, the waves have their origin in electron transfer across the electrode boundary, whereas tensammetric waves are due to adsorption-desorption equilibria at the electrode-solution interface, without electron transfer.

It is the object of the present communication to discuss briefly A.C. waves obtained when a surface active substance is not added to the electrolyte, but is formed at the electrode in virtue of electron transfer. These waves are thus intermediate between A.C. polarographic and tensammetric waves, that is, the electron transfer results in the formation of a surface active substance which then gives rise to a tensammetric wave. It is proposed to call this type of wave a "transition wave".

For example, when solutions of halogen ions were subjected to A.C. polarography, the resulting waves (Fig. 1) showed characteristics distinctly different from those obtained with cations. These characteristics can be summed up as follows:

- (i) Unlike ordinary A.C. polarographic curves, the waves were narrow and sharp; the summit potential could be determined to better than ± 0.5 mV., properties generally shown by tensammetric waves.
- (ii) The base current on the *positive* side of the summit potential was considerably depressed, indicating the presence of a surface active substance at the electrode (cf. Breyer and Hacobian 1952). The fact that the base current is decreased on the positive side of the summit potential and towards the lower part of the D.C. polarographic step, shows that the surface active substance is mercurous halide, formed at the electrode boundary by the halogen ion discharge.
- (iii) The A.C. waves of chloride and bromide ions strongly interfered with one another in the sense that the chloride wave height was considerably reduced in the presence of Br^- ions. This behaviour can be explained

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by recalling that Br^- ion is reduced at more negative potentials than Cl^- and that mercurous bromide is more strongly adsorbed at the interface than mercurous chloride. Thus bromide lowers the Cl^- wave height by displacing some of the chloride from the interface.

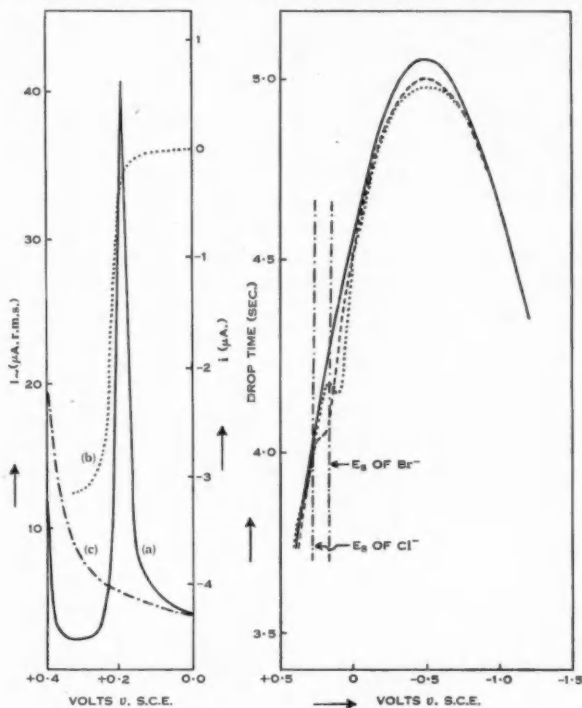


Fig. 1

Fig. 2

Fig. 1.—(a) A.C. polarogram of 10^{-2}N Cl^- in $5 \times 10^{-1}\text{N HClO}_4$.

(b) D.C. polarogram of the same solution.

(c) A.C. polarogram of supporting electrolyte ($5 \times 10^{-1}\text{N HClO}_4$).

Fig. 2.—Drop time-potential curves.

(a) ——— $5 \times 10^{-1}\text{N NaClO}_4 + 5 \times 10^{-2}\text{N HClO}_4$.

(b) - - - - as in (a) + 10^{-2}N Cl^- .

(c) . . . as in (a) + 10^{-2}N Br^- .

All potentials are referred to the saturated calomel electrode.

Drop time-potential measurements were then carried out in order to prove that adsorption-desorption processes occur at the electrode in the potential region corresponding to the formation of mercurous halide. The results confirmed the conclusions set out above (Fig. 2). A distinct kink appeared in the potential region corresponding to the halide ion discharge showing the formation of a surface active substance at the electrode boundary.

The waves are thus the outcome of two processes occurring simultaneously :

(a) The polarographic process, that is, the formation of mercurous halide in the equilibrium reaction



and

(b) The tensammetric process, given by



It is obvious that process (2) depends on the formation of mercurous halide and consequently the value of the summit potential (E_s) and wave height are determined entirely by those factors which influence equilibrium (1) and which have been discussed in detail in a previous paper (Breyer and Hacobian 1951b).

Work in progress at present in this Laboratory on A.C. polarography of organic compounds has shown that many of the waves obtained are of the transition type. Details of these investigations will be published in due course.

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ON THE DESIGN OF AN A.C. POLAROGRAPH*

By B. BREYER,† F. GUTMANN,‡ and S. HACOBIAN†

Numerous enquiries have been received by the authors regarding the design of an A.C. polarograph. The following note gives the details of a circuit used by us in previous work (Breyer, Gutmann, and Hacobian, 1950a, 1950b, 1951; Breyer and Hacobian, 1951a, 1951b).

Figure 1 shows the polarizing circuit consisting of the polarographic cell, C , the potentiometer P (40 ohms or less) as source of D.C. potential, and a potentiometer V for regulating the small superimposed sinusoidal potential (scanning voltage). The superimposed A.C. voltage V is stabilized by using a constant voltage regulator (magnetic type). Odd harmonics produced by the constant voltage transformer are innocuous.

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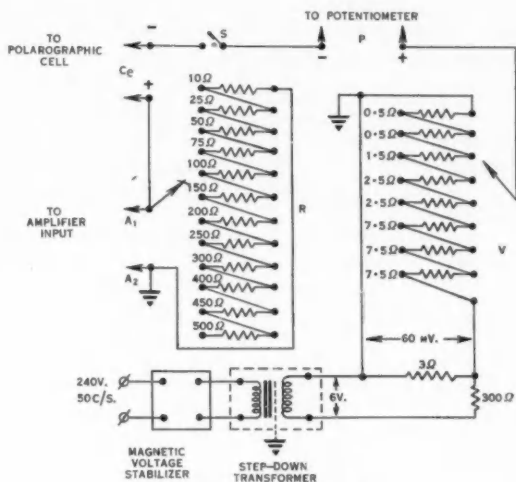


Fig. 1.—The polarizing circuit.

C_p , to polarographic cell; S , on-off switch; P , to potentiometer; V , A.C. voltage input (all resistors non-inductively wound); T , step-down transformer: input 240 V., output 6 V.; M , magnetic voltage stabilizer; $A_1 A_2$, to amplifier input; R , voltage dropping resistors.

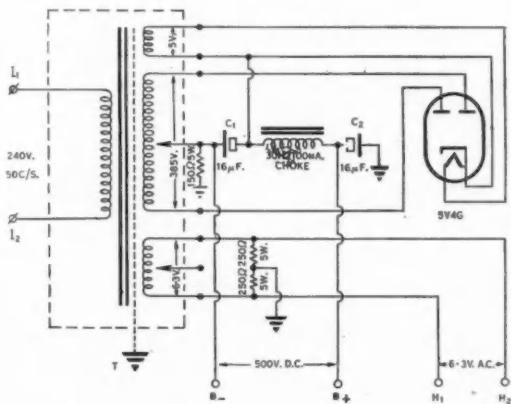


Fig. 2.—The power pack.

$I_1 I_2$, 240 V., 50 c/s. regulated A.C. input; T , multiple-ratio transformer with electrostatic shield between primary and secondary: input, 240 V., output, 5 V. (3A.), 385 V., C.T. (120 mA.), 6.3 V., C.T. (5A.); $C_1 C_2$, 16μF. electrolytic condensers (800 V. peak).

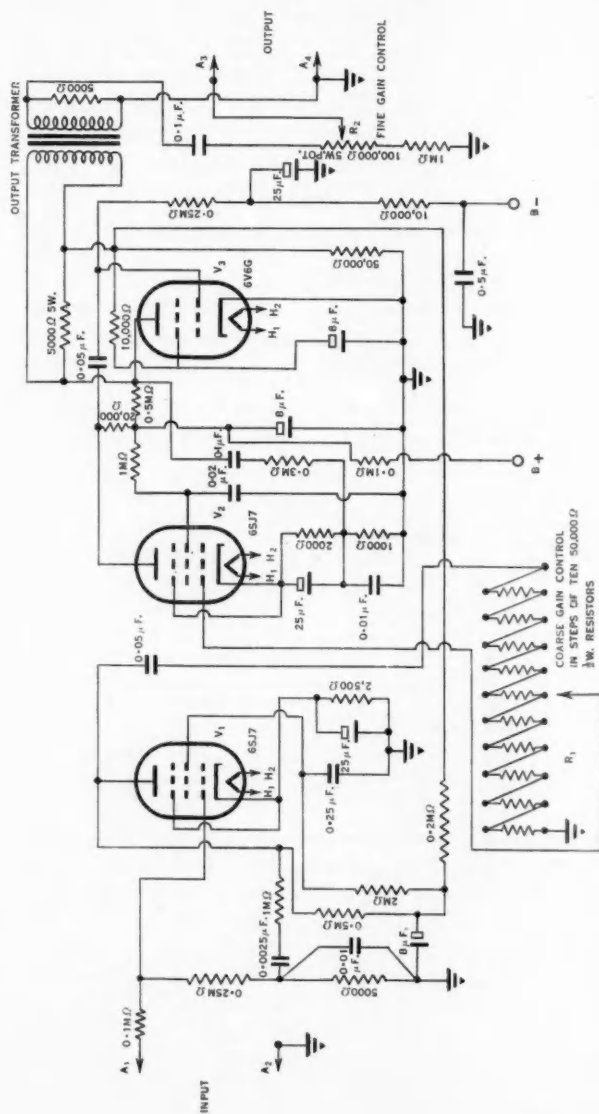


Fig. 3.—High gain amplifier.

$A_1 A_2$, input of amplifier; $A_3 A_4$, output of amplifier; R_1 , coarse gain control in steps of ten 50,000Ω, ½W. resistors; R_2 , fine gain control, 100,000Ω, 5W. potentiometer; $V_1 V_2$, 6SJ7 valves; V_3 , 6V6G valve. All resistors ½W. except when stated otherwise; electrolytic condensers 525V. peak.

The amplifier input, A_1A_2 , is suitably controlled by a set of voltage dropping resistors R . The A.C. voltage across A_1A_2 is amplified by means of a conventional high gain amplifier (Fig. 3) whose operating voltages are supplied from the power pack (Fig. 2). The amplifier is resistance-capacity coupled; the first and the second stage using two 6SJ7 valves and the output stage a 6V6G valve coupled to a suitable output transformer. Coarse and fine gain controls are provided: the coarse control is effected by means of the voltage divider R_1 with 10 fixed settings, controlling the input to V_2 , while the fine control operates by means of a continuously variable potentiometer R_2 in the output circuit (see Fig. 3).

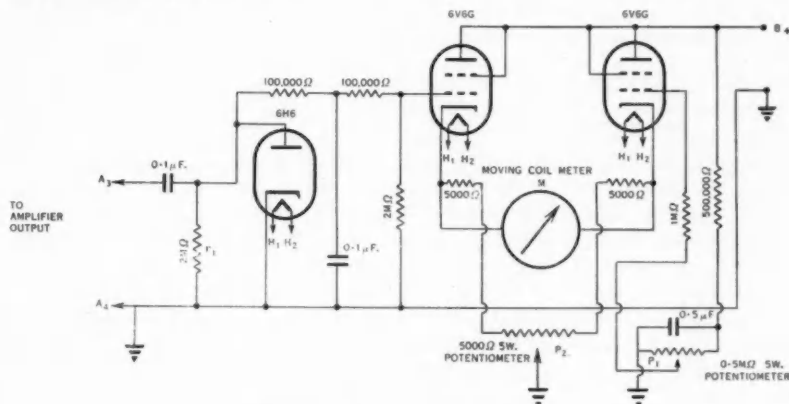


Fig. 4.—Vacuum-tube voltmeter.

A_2A_4 , to amplifier output; M , 50–100 μ A. full-scale deflection moving coil meter and circular-scale graduated 0–100 mm.; P_1 , coarse zero control, 500,000 Ω , 5W. potentiometer; P_2 , fine zero control, 5000 Ω , 5W. potentiometer; r_1 , 2M Ω (all resistors $\frac{1}{2}$ W.).

The output of the amplifier appears across a load resistor r_1 (Fig. 4) which is in parallel with a 6H6 diode rectifier. The rectified voltage is applied to the grid of a conventional D.C. single-stage vacuum-tube voltmeter employing two 6V6G valves in a balanced circuit. A moving coil meter M , 50–100 μ A. full-scale deflection, measures the A.C. polarographic differential currents. Before these readings are taken, the zero of the instrument is set by means of the potentiometers P_1 (coarse zero control) and P_2 (fine zero control), whilst switch S (Fig. 1) is in the open position. A peak smoothing arrangement (cf. Breyer, Gutmann, and Hacopian 1950a) can be incorporated in the design of the vacuum-tube voltmeter.

Proper screening of the cell circuit and adequate shielding of grid current leads is essential. Good earthing of the instrument must be ensured or errors due to stray pick-up are liable to become excessive.

The authors are indebted to the Trustees of the Science and Industry Endowment Fund for a research grant.

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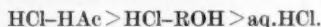
THE HYDROLYSIS OF ACETONE-2,4-DINITROPHENYLHYDRAZONE*

By C. M. STEWART†

As it is frequently necessary to recover a carbonyl compound from the hydrazone (for instance, after chromatographic separation of a mixture), the hydrolysis of acetone-2,4-dinitrophenylhydrazone was examined with a view to establishing conditions under which side reactions would be suppressed and a high yield of the ketone obtained.

Dicarbonyl compounds have been shown to be effective in regenerating aldehydes and ketones from their hydrazones by double decomposition (Strain 1935) and pyruvic acid, particularly, was examined by Fischer and Ach (1889).

Johnson and Stieglitz (1934) have shown that, in the hydrolysis of benzophenonehydrazone with either hydrochloric acid and acetic acid or with hydrochloric acid and a lower monohydric alcohol, the relative efficiency in preventing the formation of a ketazine is as follows:



When acetone-2,4-dinitrophenylhydrazone was hydrolysed with these solutions analogous results were obtained (Table 1).

TABLE I

Reaction Mixture	Time of Refluxing before Distillation (hr.)	Acetone Reformed (Corrected) (%)
1.07N HCl (250 ml.)		
with glacial acetic acid (250 ml.) ..	2	68.5
" " " " " " ..	5.5	59.5
with propanol (250 ml.)	2	56.5
with water (250 ml.)	2	52.3
" " " " " " ..	4	41.0

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Inorganic buffer solutions were examined and it was found that a maximum rate of acetone regeneration occurred at pH 2, the acetone liberated amounting to some 94 per cent. 2N Hydrochloric acid and the constant boiling solution of the acid were also examined. The rôle of hydrochloric acid may be explained by a mechanism similar to that proposed by Johnson and Stieglitz (1934). It may be concluded, from the data in Table 2, that a high yield (94 per cent.) of acetone from its 2,4-dinitrophenylhydrazone is obtained by heating the hydrazone with (a) an aqueous solution containing a slight excess of pyruvic acid, or (b) an aqueous solution of an acid having pH 2.

Experimental

Acetone-2,4-dinitrophenylhydrazone was prepared by the method of Iddles and Jackson (1934) in 96% yield, m.p. 126.5°C.

In determining the efficiency of hydrolysis in the experiments the liberated acetone was distilled, from the reaction mixture in a 1 l. flask (in some cases after refluxing for a time), into an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2N hydrochloric acid. The resulting hydrazone was collected on a sintered glass crucible (2G4), washed, and dried to constant weight in a vacuum desiccator. Control experiments in which acetone was distilled from hydrochloric acid solution indicated that a correction factor of +3.6% was necessary to give quantitative recovery. The results (Table 1) support the previous observations of Johnson and Stieglitz (1934). In each experiment 0.8 g. of acetone-2,4-dinitrophenylhydrazone was used.

TABLE 2

No.	pH	Acetone Reformed (Corrected) (%)	Remarks
1	8.0	7.9	
2	6.9	26.8	Acetone distilled off for 1 hr.
3	6.9	28.0	" " " for a further hr.
4	6.9	86.2	Distillation continued (5 hr.) until no more acetone distilled over
5	5.2	42.4	
6	3.2	84.7	
7	2.0	93.6	
8	1.4	92.8	
9	0.9	78.2	
10	Neg.	83.9	2N HCl for reaction mixture
11	Neg.	86.3	Constant boiling HCl for reaction mixture
12	—	93.9	A slight excess of pyruvic acid plus water to bring total volume to 500 ml.
13	13	69.5	c. N/10 NaOH solution

Several hydrolyses were carried out using buffered solutions (made up from primary and secondary phosphates and hydrochloric acid), the pH's of which were checked with a quinhydrone electrode. Acetone was distilled for 1 hr. (except in Nos. 3 and 4) from the reaction mixture without prior refluxing, the volume being maintained at 500 ml. by the addition of water, or constant boiling hydrochloric acid in one case (No. 11). The m.p. of the reformed acetone-2,4-dinitrophenylhydrazone was within the limits $126.5 \pm 0.5^\circ\text{C}$. In one case (No. 13) a white crystalline substance, having m.p. 90°C ., separated in the condenser and was probably *m*-dinitro-

benzene (Macbeth and Price 1937). In each experiment 1.0 g. of acetone-2,4-dinitrophenyl-hydrazone was used, and the results are recorded in Table 2.

This work was carried out in 1939 as part of the research programme of the Department of Chemistry, University of Otago, New Zealand.

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